

Research and Development

PROCEEDINGS:

POLLUTION PREVENTION CONFERENCE ON LOW- AND NO-VOC COATING TECHNOLOGIES

Prepared for

Office of Pollution Prevention and Toxics

Prepared by

Air and Energy Engineering Research Laboratory Research Triangle Park NC 27711

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PROCEEDINGS:

POLLUTION PREVENTION CONFERENCE ON LOW- AND NO-VOC COATING TECHNOLOGIES

May 25 through 27, 1993 San Diego, California

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POLLUTION PREVENTION CONFERENCE ON LOW- AND NO-VOC COATING TECHNOLOGIES

Sponsored by:

U.S. ENVIRONMENTAL PROTECTION AGENCY
AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
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POLLUTION PREVENTION PROGRAM

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and

AMERICAN INSTITUTE FOR POLLUTION PREVENTION

UNIVERSITY OF CINCINNATI

CINCINNATI, OH 45221

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INTRODUCTION

Surface coating operations release approximately 19 percent of stationary area source volatile organic compound (VOC) emissions¹. Many of these sources cannot be impacted by add-on controls at a reasonable cost due to their small size and/or the difficulty of capturing emissions. The reduction of solvent emissions from architectural and other coatings continues to rely on prevention technologies, such as the replacement of VOC with water or nonphotochemically reactive solvents, the use of high solids coatings, or improvement of the efficiency of transfer of the coating to the coated surface. In current practice, reformulation with nonphotochemically reactive solvents may lead to other environmental problems, such as increased toxicity, greater stratospheric ozone depletion potential, and worsened multimedia effects.

A conference titled, "Pollution Prevention Conference on Low- and No-VOC Coating Technologies," was held on May 25 through 27, 1993 in San Diego, California. The conference was sponsored by the U.S. Environmental Protection Agency (EPA), Research Triangle Institute (RTI), and the American Institute for Pollution Prevention (AIPP). The primary purpose of the conference was to provide a forum for the exchange of technical information on coating technologies. Specifically, the conference was designed to focus on improved and emerging technologies that result in fewer VOC and toxic air emissions than traditional coating systems.

Approximately 230 people attended the conference. Of these attendees, about 50 percent were from industry, 40 percent from government, and 10 percent from consulting firms and universities. There were nine foreign registrants: three each from Taiwan and the United Kingdom; and one each from Sri Lanka, Norway, and the Philippines. Conference registrants are listed in Appendix A.

Technical papers presented at the conference were divided into 11 sessions focusing on different topical areas including coating technologies, specific coating applications and case studies, application equipment, and pollution prevention concepts. Several papers focused on new products and improvements in these areas, such as an electrophoretic urethane coating from Great Britain, a zero-VOC house paint from Glidden, and developments involving inorganic polymers such as zinc silicates and silicones. Coatings for substrates, such as metal (aerospace), wood (furniture), plastic, foil, and concrete, were also discussed.

¹U.S. Environmental Protection Agency. 1993. Regional Interim Emission Inventories (1987-1991), Volumes I and II. EPA-454-R-93-021a and EPA-454-R-93-021b. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. May.

SESSION 1

OPENING

WELCOME ADDRESS

by
Richard J. Sommerville
Air Pollution Control Officer
San Diego County Air Pollution District
San Diego, California

KEYNOTE

"A Manufacturing Company's View of Low VOC Coatings"

by

Paul Eisele

Director of Health, Safety & Environmental Affairs

Masco Corporation

Taylor, Michigan

PAPERS PRESENTED:

"Coatings Research in the U.S. EPA's Organics Control Branch"

Michael Kosusko

U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, North Carolina

"Using Life Cycle Analytical Techniques to Assess Alternative Coating Systems"

by A

Keith A. Weitz

John L. Warren (Speaker)

Research Triangle Institute

Center for Economics Research

Research Triangle Park, North Carolina

WELCOME ADDRESS

by

R. J. Sommerville

As the air pollution control officer for San Diego County, I'm gratified to see an entire conference devoted to pollution prevention. It's in all of our best interests to eliminate pollution at the source.

Effective prevention measures can reduce the need for stricter regulations in the future.

We've all heard a lot of talk lately about how the cost of regulations in California are chasing businesses away. The simple fact is that California is a leader in air pollution regulations-because it's a leader in producing smog. California is home to 3 of the 10 smoggiest cities in the country. Environmental regulations are one of the compromises we make in order to continue living and working in one of the best climates in the world.

But that doesn't mean we can't do things better. At the San Diego Air Pollution Control District, my staff has literally spent hundreds of hours with business owners and the military to gather their input on everything from rule development to permit program streamlining.

Fortunately, California has become a pioneer in producing low-volatile organic compound (VOC) and VOC-free coatings. Also, coating manufacturers are currently marketing products that exceed regulations in anticipation of stricter rules in the future.

Individual companies are also taking the initiative to reduce or eliminate the use of coatings that contain VOCs. For example, BASF has developed a new VOC-free, water-based adhesive bonding primer for the aerospace industry. The company is also developing VOC-free, air-dried primers which could possibly be used in conventional metal shops. Another company has begun using powder coatings as a substitute for high-VOC, high-performance architectural coatings.

Southern California Edison of Irvindale, California has created a Customer Technology Application Center. The center features a demonstration facility and educates industry about low-VOC coatings, new spray equipment, and new curing methods including ultraviolet, radio-frequency, and infrared materials. Its staff works with painters to assist them in converting to water-based and high-solid coatings.

The center has also made a lot of progress in finding solutions to meet the needs of individual companies, particularly in the area of water-based wood product coatings. The low-VOC, water-based coating now produces a more durable finish than standard lacquer. One user accidentally spilled his coke over a piece of furniture he was working on. The soda was left on the wood overnight and didn't even make a mark.

Throughout the conference today and tomorrow, you will have the opportunity to learn about other developments in VOC-free and low-VOC coating technologies and products, as well as new applications for them. Please keep in mind that your air quality district is there to help you adapt to these new coating methods. Don't hesitate to use our expertise to help make your lives easier and your businesses more successful. We're on the same team. Thank you very much.

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

A MANUFACTURING COMPANY'S VIEW OF LOW VOC COATINGS

Paul J. Eisele
Director Health, Safety & Environmental Affairs
Masco Corporation

Introduction

Any discussion of low VOC coatings must have a ground work laid to determine the perspective of the presenter. Masco Corporation and its sister company MascoTech (formerly Masco Industries) are manufacturers of consumer products and industrial products respectively. Masco Corporation is the largest manufacturer in the U.S. of furniture and kitchen cabinets, thus wood products. Masco is also the largest manufacturer of plumbing products, faucets, tubs and spas. MascoTech is a leading manufacturer of automobile parts and architectural products like windows and doors. I stress that Masco is a manufacturer concentrating on manufacturing processes for simple products. Forbes Magazine called Masco "Masters of the Mundane". I say all this to preface the fact that we focus on making simple products better. Coatings are an important component of many of our products. Finishing in the Masco "mind" varies from electroplating of brass, coating metal doors, painting plastic auto parts to finishing wood. Masco is not a finish supplier but rather a coating user. The Company expects most coating R & D to be done by its suppliers not in our R & D labs. We do however invest considerable time in testing application, durability and performance of coatings within the divisions like Delta Faucet and Drexel Heritage Furniture. The Company does strive to reduce emissions of VOC and air toxics through a fairly standard mix of pollution prevention, control equipment and coating application.

Pollution Prevention

The Company has approached pollution prevention as both a cost saver and regulatory initiative. From a regulatory standpoint the Pollution Prevention Act fit into our existing programs in media specific regulatory initiatives in the Clean Air Act and CERCLA for example (Figure 1). In addition the Company was asked by the USEPA to participate in the voluntary Industrial Toxics Program also known as 33/50. The Program calls for voluntary reductions in emissions of some seventeen toxic compounds by 33% in 1992 and 50% by 1995. Many of the target compounds are also VOC's including xylene, toluene, methyl ethyl ketone and methyl isobutyl ketone which are also common solvents in coatings. Both Masco companies achieved greater than 33% reductions through 1992 (Figure 2). The greatest reduction in Masco Corporation was made by the Home Furnishing divisions which include furniture and fabric manufacturing (Figure 3). The reductions result from such factors as use of higher transfer coating application technologies such as high volume low pressure (HVLP) spray guns, limited use of water borne coatings, and improved manufacturing process resulting in lower rework and cleaning. The greatest reduction in MascoTech was made by the Architectural Product group

which include door and window manufacturing (Figure 4). Most of the reductions were achieved by use of waterborne coatings and glues or powder coating on metal parts, as well as purchase of precoated steel. The Companies have found greater applicability of waterborne coatings to metal because the substrate can be made more uniform for water coatings than can other substrates like wood or plastic.

Low VOC Coatings

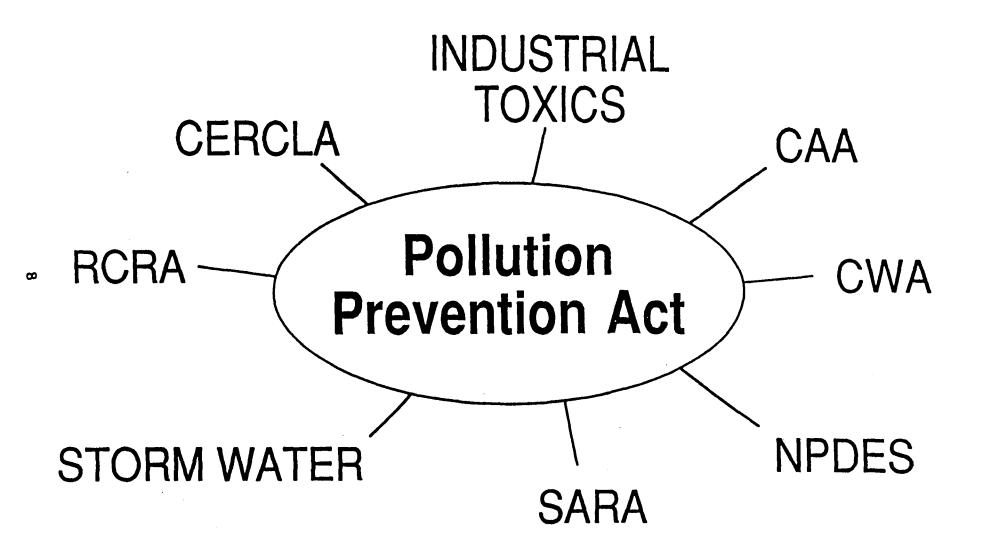
Masco generally relies on the marketplace for new coating technologies, that is, we do not attempt to develop our own coatings. Advances are a result of collaborative efforts between the Company and finishing suppliers. This is very typical of manufacturers. In some instances the product may dictate extensive R & D to use lower VOC coatings. One such example is automotive headlight manufacturing done by MascoTech Coatings. Industry demands for light weight vehicles without sacrificing safety have led to utilization of composite materials in autos. The coating demands are great since in some instances they play an important role in the function. MascoTech uses silicon to coat poly carbonate lenses as well as UV inhibitor to prevent cracking to give the plastic the properties of glass. The plastic light housing is vacuum metalized and then conventionally topcoated to give the reflective properties. The resulting head or tail lamp assembly is much lighter than the old assembly made of glass and metal with no loss of quality. Vacuum application is very efficient, as low to no VOC materials can be used. MascoTech coating is now experimenting with a high solids base and top coat applied in the vacuum chambers. There have been numerous problems in the fouling of the vacuum chambers to date but when perfected this will drastically reduce VOC emissions.

The use of low VOC materials for wood coating has also been challenging. Lexington Furniture, a Masco Corporation company began attempting to use waterborne coatings in the late 1980's in production. To date its success has been on particular wood species, and finishes which do not require smooth, rich finishes, for example wicker, rattan and one oak suite. Since that time more lower VOC coatings are being used in production but still limited to particular woods and particular fashion looks. Wood is a difficult substrate because of its porosity, non uniformity of substrate, swelling when moist, and inability to apply high temperature drying. Henredon Furniture has had some success with a couple of suites. Universal Furniture is testing a reverse hybrid system, that is where waterborne stains or color coats are used followed by coating with traditional nitrocellulose lacquers sealer and topcoats. This means changes to conventional finishing in that extensive wiping and sanding must be done making it more labor intensive manufacturing. It does have the advantage of achieving VOC reductions without the disadvantage of difficult repair or rework. Most waterborne coating approaches had utilized conventional stains on wood followed by waterborne sealers and topcoats. A major problem has been rework or repair because waterborne topcoats are not as amenable as conventional nitrocellulose which is very forgiving and easy to remove or rework with VOC solvents. This is especially frustrating for a wood furniture piece with extensive value added prior to finishing.

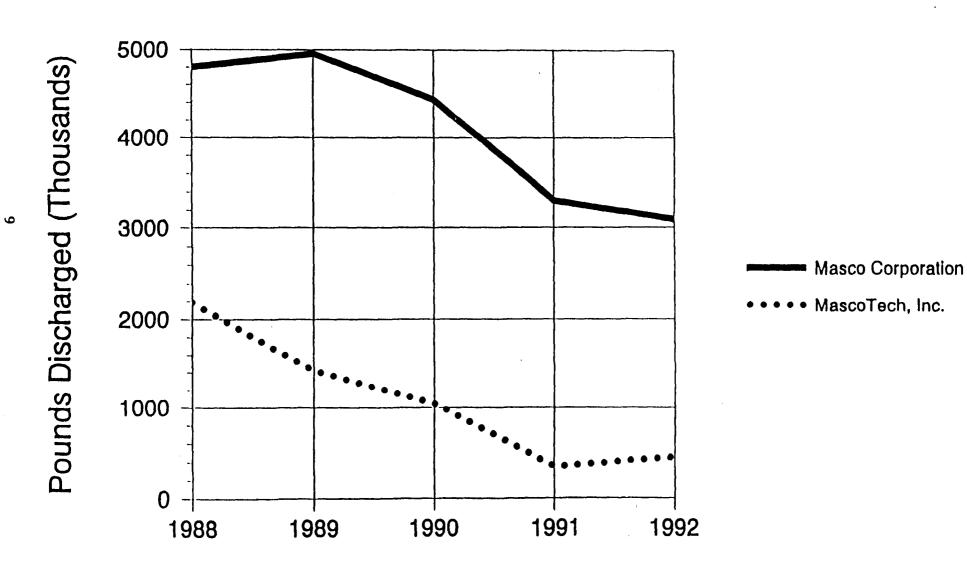
Summary

Masco like many other manufacturers has found it easier to utilize low VOC coatings on metal products rather than plastic or wood. Both plastic and wood are not uniform substrates

for finishing materials and are susceptible to damage with high temperature drying or setting. The Companies, both Masco Corporation and MascoTech, have had far greater success to date in reducing VOC's by a combination of better solvent management, improved application technologies and some use of conventional controls rather than by low VOC coatings for non metal materials. With more research on finishing material chemistry and application, low VOC coatings will become a bigger share or "piece" of the VOC reduction "pie". Activities like this workshop are necessary to insure that recent advances are known and understood so that they can be assimilated into the mainstream of manufacturing. Some of us wish that low VOC coatings were available and usable for all of products now. The Company and its suppliers are committed however to continuous improvement in its products and manufacturing processes to utilize the complete mix of technologies to reduce VOC and toxic emissions, which in the future will be achieved through greater reliance on low VOC coatings.

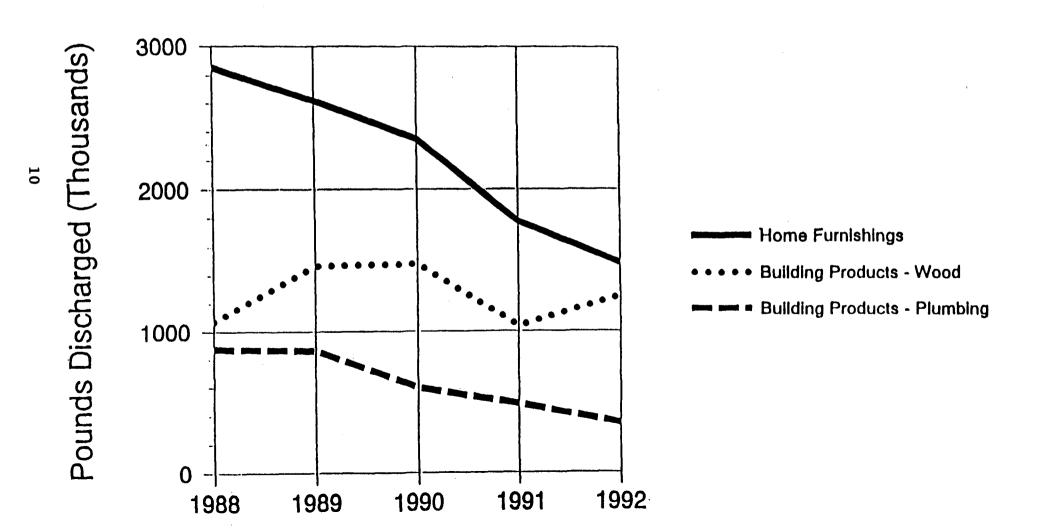


MASCO TOXICS PROGRAM

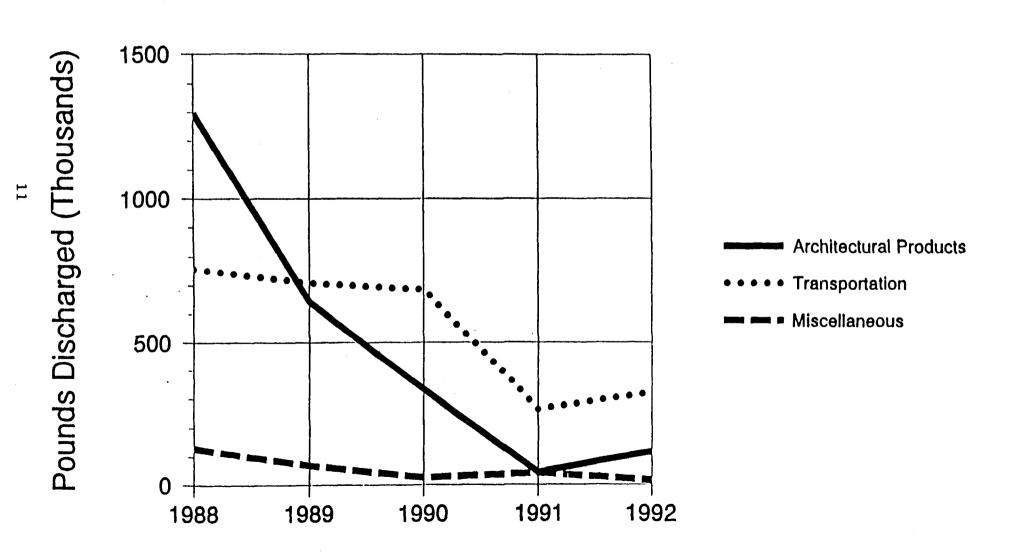


MASCO CORPORATION

TOXICS REDUCTION PROGRAM



MASCOTECH, INC. TOXICS REDUCTION PROGRAM



COATINGS RESEARCH IN THE U.S. EPA'S ORGANICS CONTROL BRANCH

by

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ABSTRACT

This paper provides a brief overview of research and development projects in the Organics Control Branch of the U.S. Environmental Protection Agency's Air and Energy Engineering Research Laboratory that impact on surface coating processes. Projects can be characterized as: (1) scoping studies, in which an industry or process is characterized and pollution prevention (P2) opportunities are identified; (2) technology assessment and development projects, in which the feasibility of specific coating technologies or P2 techniques is evaluated; (3) demonstration projects, in which methods of reducing emissions are tested in cooperation with industrial partners: or (4) technology transfer projects, such as this conference. Scoping projects are ongoing for paper and other webs (surface coating), furniture restoration and repair, printing, architectural and industrial maintenance coatings, consumer/commercial adhesives, and roofing. Technology assessment and development projects are ongoing to evaluate very low-VOC, non-waterborne coatings and a 2-component epoxy topcoat for wood furniture manufacturing, to identify technical barriers to the use of radiation-cured and waterborne coatings, and to assess innovative ink-feed systems for printing. Demonstration projects are planned for auto body refinishing, for coated and laminated substrate manufacturing (i.e., the use of aqueous adhesives and of alternative equipment cleaning methods), and for the design of recirculating spray booths incorporating VOC concentration gradient phenomena.

(This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.)

INTRODUCTION

*For more than two decades, the U.S. Environmental Protection Agency's (EPA) Air and Energy Engineering Research Laboratory (AEERL), located in Research Triangle Park, North Carolina, has been exploring control approaches for the pollutants and sources that contribute to air quality problems. AEERL has successfully developed and demonstrated cost-effective sulfur dioxide, nitrogen oxides, and particulate control technologies for fossil fuel combustion sources. More recently, it has expanded its interest to areas that include indoor air quality, radon, organic control, stratospheric ozone depletion, and global warming. The AEERL also develops inventories of many types of air emissions. Over the past several years, AEERL has made a substantial effort to expand pollution prevention as the preferred choice to reduce air emissions. Its goal is to conduct research that will result in the greatest possible reduction of air pollution for the lowest cost.*1

The Organics Control Branch (OCB) of AEERL is charged with developing and assessing pollution prevention (P2) techniques and addon control technologies for reducing organic air emissions; i.e., organic air toxics (hazardous air pollutants [HAPs]) and volatile organic compounds (VOCs). OCB's P2 research is focused in three technical areas: (1) Surface Coating, such as wood furniture finishing, printing, and the use of adhesives and radiation-cured coatings; (2) Solvent Cleaning, such as vapor degreasing, process equipment cleaning, and in-process precision cleaning; and (3) Consumer/Commercial Products (C/CP), including traditional consumer products (e.g., hair spray and household cleaners) and non-process solvent use in commercial operations such as textile manufacturing, roofing, and furniture refinishing. Each of the industries with which OCB is working has concerns about emissions from each of OCB's technical areas. Most of these industries use surface coatings, use solvents (to prepare surfaces for coating or to clean equipment), and use a wide variety of prepackaged commercial products in their facilities. This paper will discuss OCB's projects that impact surface coating operations. Projects and project contacts are provided Appendix I.

Generally, projects in the Organics Control Branch can be divided into four categories:

- (1) Scoping Studies characterize an industry or process and its emissions and identify P2 opportunities to reduce those emissions. Scoping projects are ongoing for furniture restoration and repair, paper and other webs coating, printing, roofing, architectural and industrial maintenance (AIM) coatings, and consumer/commercial adhesives.
- (2) Technology Assessment and Development Projects evaluate the technical and economic feasibility of specific coating technologies or P2 techniques. Technology assessment and development projects are ongoing to evaluate very low-VOC, non-waterborne coatings and a two-component epoxy topcoat for wood

furniture manufacturing, to identify technical barriers to the use of radiation-cured and waterborne coatings, and to assess innovative ink-feed systems for printing.

- (3) Demonstration Projects investigate methods of reducing emissions in cooperation with industrial partners. Demonstration projects are in the works for coated and laminated substrate manufacturing, for the design of recirculating spray booths incorporating VOC concentration gradient phenomena, and for auto body refinishing.
- (4) Technology Transfer Projects: Such as this conference, The Pollution Prevention Conference on Low- and No-VOC Coating Technologies, or the development of information manuals or software evaluating prevention alternatives.

SCOPING STUDIES

Consumer/Commercial Products (C/CP) Report to Congress (RTC) Support

Information on non-process solvent use was evaluated for 15 industrial and commercial source categories to characterize VOC emissions and identify P2 opportunities. Non-process solvents are used by industry, commercial operations, and/or individual consumers; they are not incorporated into a product or chemically modified as part of the manufacturing process. Project results will support a Report to Congress, required by §183(e) of the Clean Air Act Amendments of 1990 (CAAA), which addresses emissions of VOCs from consumer or commercial products. Successful P2 approaches will support regulatory efforts resulting from the Report to Congress.

As a result of this evaluation, five categories were selected for further study. These categories are:

- 1) Textile Manufacturing
- 2) Furniture Repair and Refinishing
- 3) Roofing
- 4) Mold Release Agents, and
- 5) Heating, Ventilation and Air-Conditioning (HVAC) Coil and Parts Cleaning.

For each category, a more detailed evaluation of emissions, emission sources, and P2 opportunities is being completed. Three of these categories--Furniture Repair and Refinishing; Roofing; and Textile Manufacturing (e.g., screen printing)--use surface coatings. Reports detailing emissions and P2 opportunities for the five categories are expected during Fall 1993.

Assessment of Pollution Prevention (P2) Opportunities in Five Industries

In this small cooperative project with the South Coast Air Quality Management District (SCAQMD), emissions and P2 opportunities have been assessed for five industries, all of which use surface coatings: (1) Architectural and Industrial Maintenance (AIM) Coatings; (2) Consumer/Commercial Adhesives; (3) Rotogravure Printing; (4) Flexographic Printing; and (5) Graphic Arts. The final report for this project is expected during Fall 1993.

Source Reduction Review Program (SRRP) Focus Groups

The objective of the Source Reduction Review Program (SRRP) is to ensure the consideration of P2 options during the development of air toxic (also known as Maximum Achievable Control Technology [MACT]) regulations for 17 of the many source categories to be regulated under Title III of the CAAA by the year 2000. The purpose of this project is to identify P2 opportunities via focus group input for five of these categories. Of the five, only one is a surface coating category (i.e., Paper and Other Webs). The other categories are: (1) Reinforced Plastics (Boat Building); (2) Integrated Iron and Steel Manufacturing; (3) Plywood/Particle Board Manufacturing; and (4) Acrylic/Modacrylic Fiber Production. Focus groups will include the participation of industrial, governmental, and academic experts in order to get as broad a perspective as possible. The Paper and Other Webs focus group is scheduled to meet before September 30, 1993, as are the Reinforced Plastics and Iron and Steel focus groups.

TECHNOLOGY ASSESSMENT AND DEVELOPMENT PROJECTS

Wood Furniture Finishing

Status and Future Developments in Very Low-VOC Coatings. The objective of this project is to establish the status of research and development (R&D) and market development for very low-VOC coatings used for wood furniture finishing. Information will be gathered through contacts with resin suppliers, paint manufacturers, wood furniture manufacturers, and their trade associations. The question, "What is really available in terms of low-VOC coatings?" will be addressed as will the status of ongoing development projects. The technical barriers and concerns of industry about these coatings will be identified and addressed. Opportunities for demonstrating very low-VOC coatings for wood furniture finishing will be identified. The final report for this project should become available during the Fall of 1993.

Waterborne Two-Component Epoxy Topcoats. Details of this project will be presented on Wednesday afternoon, May 26, 1993, at this conference. The paper will be available in the conference proceedings (pages 357-365). This project is cooperatively funded with SCAQMD. A two-component water-based epoxy resin coating system containing less than 0.08 lb/gal (10 g/l) VOC has been developed as both clear and white-pigmented topcoats. These topcoats have met most performance criteria including: (1) a VOC content of less than 0.08 lb/gal; (2) high gloss; (3) dry to touch in 10 minutes or less, dry to handle in 15 minutes or less; and (4) a 2H pencil hardness.

<u>Technical Barriers to the Use of Radiation-Cured and Waterborne</u> Coatings

This project is part of SRRP and is just underway. The use of radiation-cured (e.g., ultraviolet [UV]-cured and electron beam [EB]-cured) or waterborne coatings is a P2 option for several SRRP source categories. However, technical barriers to their broadened usage such as concerns about toxicity and the difficulty of coating complex parts using radiation-cured coatings exist. The objective of this project is to identify and characterize these technical barriers and to identify and complete critical research to overcome them.

Innovative Ink Feed Systems

This project is also part of SRRP and is just underway. The systems (e.g., piping, tanks, and mixers) used to feed ink to printing presses and their subsequent cleaning requirements are the source of substantial volatile organic HAP emissions. Substitute ink feed systems could substantially reduce these emissions.

DEMONSTRATION PROJECTS

Auto Body Refinishing

This project is being completed cooperatively with SCAQMD. Its objective is to demonstrate a P2 technique or techniques to reduce volatile organic emissions from auto body refinishing operations. Although project details have not yet been finalized, we will probably work with a university-based paint research center to field- or pilottest innovative, low- or no-VOC coatings that have been proven at the bench-scale. Work is expected to be underway during 1993.

Retrofit of Existing Solvent-based Flexible Substrate Coating Equipment to Use Water-based Coating Systems

The coated and laminated substrate manufacturing industry makes a wide variety of pressure sensitive products such as masking, cloth (duct), and cellophane tapes, tags, labels, and a number of exotic laminated products. It was selected for study because of significant air emissions of methyl ethyl ketone (MEK) and toluene reported in the 1990 Toxics Release Inventory System (TRIS)²; i.e., it is the #1 source for MEK (8,050 tons[7,300 Mg]) and the #3 source for toluene (13,000 tons[11,800 Mg]). A focus group, including members of the Pressure Sensitive Tape Council (PSTC) and the Tag and Label Manufacturers Institute (TLMI), and academic and state environmental experts, helped OCB identify opportunities for significant reductions of organic HAP emissions in this industry.

The use of solvent-borne coatings (e.g., adhesives) was identified as the primary source of the industry's toluene and MEK emissions. The key barriers to the use of waterborne coatings by small firms in this industry are: (1) The capital cost of purchasing new equipment which could use waterborne adhesives and (2) The lack of readily available technical information which would allow the retrofitting of existing solvent-based equipment to use waterborne coatings. PSTC representatives from large companies indicated that they would work with OCB to document successful applications of retrofit technology so that a descriptive "how to" manual could be developed for use by small businesses in the industry. Once the use of waterborne coatings is implemented by small businesses, significant toluene and MEK emission reductions would be achieved.

A report documenting background issues for retrofitting equipment to use waterborne coatings should become available during the Fall of 1993. The high level of industry participation through the PSTC will allow demonstration and documentation efforts to be initiated during 1993.

Partitioned, Recirculating Spray Booth

Recirculation in paint spray booths has been recognized for many

years as a means of increasing the concentration and reducing the volume of spray booth exhaust. This allows the use of a smaller add-on control device, hence reducing air pollution control costs. A partitioned, recirculating paint spray booth is shown in Figure 1. Partitioning of the spray booth exhaust stream takes advantage of the VOC concentration gradient that exists vertically across the booth exit. VOCs stratify in the booth, and their concentration is greatest closer to the floor. By pulling the booth exhaust stream from the bottom portion of the booth and the recirculating stream from the top portion of the booth, the concentration of the exhaust stream can be enhanced, perhaps reducing the exhaust volume to be controlled below that of a simple recirculating booth. Preliminary field tests have shown the feasibility of reducing controlled air volumes by 50-75% below those of non-recirculating booths.

A demonstration of the stratified recirculation concept is planned at the U.S. Marine Corps (USMC) Maintenance Depot near Barstow, California. The demonstration will be completed cooperatively with the Marine Corps and Penn State University. During the demonstration, an existing spray booth will be modified to use both recirculation and partitioning. A movable plenum will be used to evaluate the optimum height for flow partitioning. An additional control technology will be evaluated during the demonstration. Spray booth exhaust will feed to an add-on control device supplied by Terr-Aqua which uses UV light to destroy organics absorbed on a catalytic substrate, scrubbing with ozonated water, and a final activated carbon polishing step.

Paint Application Technology

Evaluation of Ultra Low Volume (ULV) Spray Gun System. The objective of this project is to evaluate an ULV spray gun system. Tests have been completed cooperatively with the U.S. Air Force at Warner-Robins Air Force Base, Georgia. Qualitative results of the test are promising. A large improvement of paint utilization efficiency was attributed to the enhanced paint lay down or flow out provided by the gun. This and the ability to spray high viscosity paints (which contain fewer solvents) have led to a 50 to 75% reduction in VOC emissions. The final project report is expected during Fall 1993.

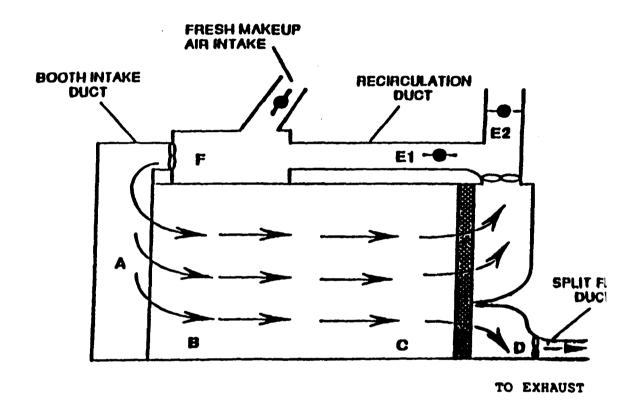


FIGURE 1. The Partitioned, Recirculating Spray Booth Concept

Spray Gun Cleaning. The purpose of this project is to compare emissions from two types of paint spray gun cleaning equipment (i.e., open and closed systems) to each other and to those from current cleaning practices. In the open system, cleaning solvent is sprayed from the gun, with its spray tip removed, into an open container that is shaped to minimize solvent bounce-back and that has air flow into the bottom of the container. The closed system consists of spraying cleaning solvent through the gun while it is enclosed in a capture device. This project, which should be completed during Fall 1993, is being done in support of EPA's Control Technology Center (CTC). The CTC provides technical support to local, state, and EPA Regional environmental personnel, small businesses, and international clients. It is co-sponsored by AEERL and EPA's Office of Air Quality Planning and Standards.

TECHNOLOGY TRANSPER

Technology transfer (T^2) is the final and, perhaps, the most important type of project activity in the Organics Control Branch. Through T2, the results of OCB's research are provided to the people who can use it, hopefully in a format that they can easily use. also provides OCB an opportunity to interact with its potential clients (i.e., through workshops and conferences) to better understand their needs and the status of technology in many industries. straightforward means of providing information to potential users are project reports and presentations at large professional conferences. However, these mechanisms are not necessarily targeted at the user community. Some of the difficulty of reaching the right audience can be overcome by providing report copies to local, state, and regional P2 and small business assistance providers, the Control Technology Center, and industry trade associations. Information can also be distributed through P2 data bases and electronic bulletin boards such as the Pollution Prevention Information Clearinghouse (PPIC) which, as part of the Pollution Prevention Information Exchange System (PPIES), is managed by EPA's Office of Environmental Engineering and Technology Demonstration.

EPA-sponsored workshops and conferences provide an opportunity for interacting directly with a targeted audience. OCB has completed two conferences for surface coatings. The Surface-Coating-Free Materials Workshop was held in July 1991, to explore the potential for development and use of materials that would not need to be coated during manufacture or recoated during use. If such materials were to come into widespread use, VOC and air toxic emissions associated with surface preparation (cleaning), coating, and paint stripping before recoating could be avoided. A summary of this workshop is available from the National Technical Information Service (NTIS)³. This is the second conference. The Pollution Prevention Conference on Low- and No-VOC Coating Technologies is being held to provide a forum for exchanging technical information on innovative coating technology and to allow EPA to interact with industry, academia, and others interested in surface coating technology.

A third coatings conference has been proposed for March 1995, with much the same objective as this conference. It would probably be held on the East Coast, in the Raleigh-Durham, North Carolina, area. A series of technology transfer workshops may also be proposed for completion during 1994 to allow OCB personnel to present the results of their research to, and to interact with, the user community.

SUMMARY AND CONCLUSIONS

The Organics Control Branch has a broad program in pollution prevention which impacts many industries ranging from wood furniture manufacturing to coated and laminated substrate manufacturing to printing and publishing. Each of these industries has common concerns. They all use surface coatings; most use solvents for preparing surfaces for coating or for cleaning equipment; and all use an abundance of prepackaged commercial products. This paper summarizes surface coating activities in OCB. Although many of its initial research products are nearing completion, OCB expects that its surface coatings program will continue to grow and develop. The input of a broad spectrum of industry, academic, and other surface coating experts, such as the attendees at this conference, is needed to continue to enhance the focus, quality, and content of OCB's current and future research activities.

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- 2. Toxic Chemical Release Inventory, National Library of Medicine Toxnet System, U.S. Environmental Protection Agency, 1990.
- Northeim, C.M., M.W. Moore, and J.L. Warren, Surface-Coating-Free Materials Workshop - Summary Report, EPA-600/R-92-159 (NTIS PB93-101160), August 1992.

APPENDIX I: SUMMARY OF OCB PROJECTS AND PROJECT CONTACTS

I.	scc	PING				
4.	A.	Consumer/Commercial Products Report to Congress				
		1. Furniture Repair & Refinishing	R. McCrillis			
		2. Roofing	J.Whitfield			
		3. Textile Manufacturing	M.Kosusko			
	В.	Assessment of P2 Opportunities in Five Industries	M.Kosusko			
	C.	Source Reduction Review Program (SRRP) Focus Groups	C.Nunez			
П.	TEC	HNOLOGY ASSESSMENT AND DEVELOPMENT				
	A.	Wood Furniture Finishing	R.McCrillis			
		 Status and Future Developments in Very Low-VOC Coatings 				
		2. Waterborne Two-component Epoxy Topcoats				
	B.	Technical Barriers to the Use of Radiation-cured and Waterborne Coatings	C.Nunez			
	C.	Innovative Ink-feed Systems	C:Nunez			
III.	DEM	ONSTRATIONS				
	A.	Auto Body Refinishing	G. Ramsey			
	В.	Retrofit of Existing Solvent-based Flexible Substrate Coating Equipment to Use Water-based Coating Systems	C.Vogel			
	C.	Partitioned, Recirculating Spray Booth	C.Darvin			
	D.	Paint Application Technology	C.Darvin			
		1. Evaluation of Ultra Low Volume (ULV) Spray Gun System				
		2. Spray Gun Cleaning				
IV.	TEC	TECHNOLOGY TRANSFER				
	A.	Surface-coating-free Materials Workshop	M.Kosusko			
	B.	P2 Conference on Low- and No-VOC Coating Technologies - San Diego	M.Kosusko			
	C.	P2 Conference on Low- and No-VOC Coating Technologies - East Coast	M.Kosusko			

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USING LIFE CYCLE ANALYTICAL TECHNIQUES TO ASSESS ALTERNATIVE COATING SYSTEMS

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INTRODUCTION

Life cycle assessment (LCA) is a holistic approach to assessing the environmental and human health burdens associated with a given product system. It seeks to reconcile technology and ecology at each stage of the life cycle of products, processes, and activities from acquiring raw materials to recycling or disposal by identifying system inputs and outputs; assessing the potential impacts of those inputs and outputs on the natural environment, human health, and natural resources; and implementing opportunities for achieving improvements. Life cycle thinking starts before the cradle (R&D, design) and goes beyond the grave (recycling, re-use).¹

This paper describes the LCA process, which can be used to assess alternative lowand no-volatile organic compound (VOC) coating systems with the objective of minimizing potential impacts to the environment and human health. In this context, LCA is useful for recognizing trade-offs between alternative coating systems that may not have eliminated environmental and human health impacts but merely transferred them to other life cycle stages.

Currently, no protocol exists for conducting an LCA. However, LCA generally consists of the following components:

Goal Definition and Scoping: Identifies the purpose and objectives of the LCA, as well as study boundaries, data needs, comprehensiveness, users of the results, and potential applications.

Inventory Analysis: Identifies and quantifies—to the extent possible—resource and energy inputs, air emissions, waterborne effluents, solid waste, and other inputs and outputs associated with a product system. This information is compiled into a life cycle inventory.

Impact Assessment: Identifies, characterizes, and values potential impacts of concern to the natural environment, human health, and natural resources associated with the inputs and outputs of a product system.

Improvement Assessment: Identifies, evaluates, and implements opportunities for environmental and human health improvements. Opportunities for improvements may be realized at any stage of the LCA process.

LCA is not necessarily a linear or stepwise process. Rather, as suggested by Figure 1, information from any component can complement information from the other components. For instance, opportunities for environmental improvements do not necessarily stem from the life cycle improvement assessment but can be realized at any stage of the LCA process. The inventory component alone may be used to identify opportunities for reducing inputs from or outputs to the environment.

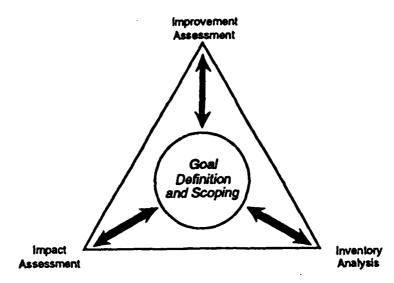


Figure 1. LCA Framework

APPLYING LCA TO EVALUATE LOW- AND NO-VOC COATING SYSTEMS

Government legislation, such as the 1977 and 1990 Clean Air Act Amendments, is the major force behind the conversion from conventional to low- and no-VOC coating systems. Another motivation for this conversion is to reduce or eliminate environmental and human health concerns associated with VOCs, such as photochemical smog and human respiratory damage.

However, switching from conventional to alternative coating systems may be exchanging one problem for another. For example, an alternative coating system may replace VOCs with other hazardous materials, or the alternative coating system may require special

drying and curing equipment that significantly increases energy usage. When switching to alternative coating systems, trade-offs besides reducing VOCs need to be evaluated. LCA may be an effective approach for assessing such trade-offs. We elaborate on the LCA process summarized in the introduction of this paper by comparing a conventional coating system with a no-VOC powder coating system. The characteristics of the two systems are as follows:

- Conventional coating system: 30 percent solids, 70 percent solvents
- No-VOC powder coating system: 100 percent solids, 0 percent solvents

Table 1 provides a comparison of the basic components of conventional and no-VOC powder coating systems.

Goal Definition and Scoping

Goal definition and scoping forms the basis of interrelationships between the inventory, impact, and improvement assessment components. As suggested in Figure 1, goal definition and scoping are both discrete activities and the basis of the life cycle inventory, impact, and improvement assessment components.

The goal definition activity clearly identifies and defines the purpose and objectives of the LCA at the beginning, as well as maintains consistency with the goals and objectives of the study throughout the LCA process. An example of goal definition, which will also be used as the guiding goal for purposes of this paper, is to assess alternative coating systems to choose the coating system that generates minimal environmental and/or human health impacts.

The breadth and depth of the LCA, or scope, is governed by the defined study boundaries, comprehensiveness, data needs, impact areas included and excluded, methodologies employed, users of results, and potential applications of the LCA (e.g., LCA as a baseline vs. comparative study). The scope of the LCA will undoubtedly be bounded by resource (i.e., money, time, technical expertise) constraints that limit the practitioner from gathering and analyzing data for each and every possible component of a system's life cycle. Thus the primary goal of scoping in this case may be to match the level of detail of the LCA with available resources while allowing the practitioner to achieve the goal of the LCA.

Because scoping may be both a discrete and integral component in LCA, it may occur at the beginning of the LCA and may be reevaluated when beginning or during the inventory analysis and the impact and improvement assessment components. For example, data required to conduct an impact assessment may be missing from the inventory component or may be of insufficient quality. In this case, the scope of the impact assessment, and thus the overall LCA, may have to be constricted.

TABLE 1. COMPARISON OF BASIC COMPONENTS OF CONVENTIONAL VERSUS POWDER COATING SYSTEMS^{2,3}

Component	Conventional Coating	Powder Coating
Basic coating inputs:		
Pigment	10–20%	40–60%
Binder (resins)	10-20%	40–60%
Carrier (solvents)	60–80%	0%
Materials pretreatment	Solvent-based primer tank(s), air dried	Anodic electrocoat tank, oven dried (475°, 5 minutes)
Application equipment	Spray booth	Spray booth
Drying	400° oven, 40–45 minutes	400° oven, 10–15 minutes
Utilization rate	60–70%	95–98%
Output waste		
Air pollution	VOCs	No VOCs
Water effluent	Waste water from equipment cleaning	Waste water from equipment cleaning
Solid waste	More packaging materials needed to protect finish	Less packaging materials needed because finish is more durable
Hazardous waste	Liquid overspray Paint sludge	Powder overspray can be easily recycled/reused.
Overhead costs	More labor More equipment to meet VOC regulations More energy costs	
Finish quality		Higher gloss Higher coatage Higher durability Higher corrosion resistance

Inventory Analysis

Life cycle inventory analysis is a technical, data-based process of quantifying energy and raw material requirements, atmospheric emissions, waterborne effluents, solid wastes, and other inputs or outputs throughout the entire life cycle of a system. Life cycle stages include raw materials acquisition, manufacturing, use/reuse/maintenance, and recycle/waste management. Figure 2 illustrates a simplified representation of the full product life cycle.

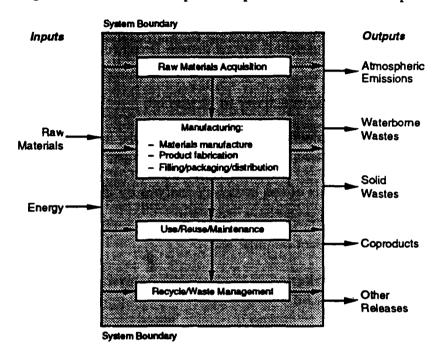


Figure 2. Simplified Full Product Life Cycle⁴

Life cycle inventory analysis is a static representation of a dynamic system, as is the entire LCA process. That is, the life cycle inventory is a "snapshot" of inputs and outputs of a given product system. In light of this limitation, some general applications of the life cycle inventory are the following:

- Establish a baseline of information on a system's overall resource and energy consumption and environmental loadings;
- Identify stages within the life cycle of a product or process where inputs and outputs might be reduced;
- Compare the system's inputs and outputs associated with alternative products, processes, or activities;
- Help guide the development of new products, processes, or activities toward a
 net reduction of resource and energy requirements and environmental
 emissions; and
- Help identify areas to be addressed during life cycle impact assessment.⁴

Because its methodology has been evolving over a 20-year period, life cycle inventory analysis is relatively well developed. We describe the steps involved in conducting the inventory analysis using the two coating systems—A (conventional) and B (powder coating)—as an example. EPA developed these eight steps for conducting an inventory analysis.⁴

- 1.) Define the Purpose and Scope of the Life Cycle Inventory Analysis. The purpose of the life cycle inventory analysis when evaluating two coating systems may be to provide baseline information for comparing the environmental and human health impacts of system A (conventional) versus system B (powder coating). The scope of the inventory analysis should, at a minimum, clearly define the following study components:
 - product, process, or activity to be studied;
 - reasons for conducting the inventory analysis, including the needs of and potential applications for pertinent user groups;
 - use of the results of the inventory analysis by the practitioner;
 - elements of the inventory analysis, such as energy and raw material inputs and waste or coproduct outputs; and
 - elements not addressed in the inventory analysis, such as socioeconomic and aesthetic issues, for example.⁴
- 2.) Define the System Boundaries. Once the goals and objectives for preparing the life cycle inventory have been determined and the intended scope identified, the practitioner can define the system boundaries. Whereas determining the scope of the inventory analysis defines both the issues and physical system to be addressed, determining the system boundaries defines the portions of the physical system that will be included in the inventory analysis. A complete life cycle inventory analysis will establish boundaries that represent the system broadly, over the entire life cycle as shown in Figure 2.

Some helpful questions for setting and describing specific system boundaries might include the following:

- Does the system need to cover the entire life cycle?
- What will the product be used for, or is the study intended to compare systems?
- What ancillary materials or chemicals are used to make or package this product or run the processes?
- In a comparative analysis, are any extra products required to allow one product to deliver equivalent or similar performance to another?

Figure 3 shows an example of the basic system boundaries for the two coating systems.

- 3.) Devise an Inventory Checklist. After defining the purpose, scope, and boundaries of the inventory analysis, the practitioner can prepare a checklist to guide data collection and to develop an inventory model. The practitioner should address eight general decision areas on the generic checklist shown in Table 2. This checklist is not definitive; the practitioner may want to tailor the checklist to meet specific needs.
- 4.) Institute a Peer Review Process. Because LCA is a fairly new concept and its methodology is not widely accepted and well-understood, LCA reviewers have recommended using a peer review process. In the context of LCA, peer review is not just a post-study activity but an integral component that is implemented early in the LCA process. In the context of inventory analysis, a peer review process may help to validate the following components:
 - scope and boundary definitions;
 - data collection and compilation plan;
 - key assumptions and value judgments, if any;
 - validity of results; and
 - interpretation and communication of results.

Checklists such as the one presented in Table 2 are useful for organizing information on these components to aid in the peer review process.

- 5.) Gather Data. Data gathered in the inventory analysis may come from a number of different sources and may be categorized in different ways. Some example data categories include the following:
 - Individual Process- and Facility-Specific: data gathered from a particular operation within a given facility
 - Composite: data from the same operation or activity combined across locations
 - Aggregated: data combining more than one process operation
 - Industry-Average: data derived from a representative sample of locations and believed to statistically describe the typical operation across technologies
 - Generic: data whose representativeness may be unknown but that are qualitatively descriptive of a process or technology

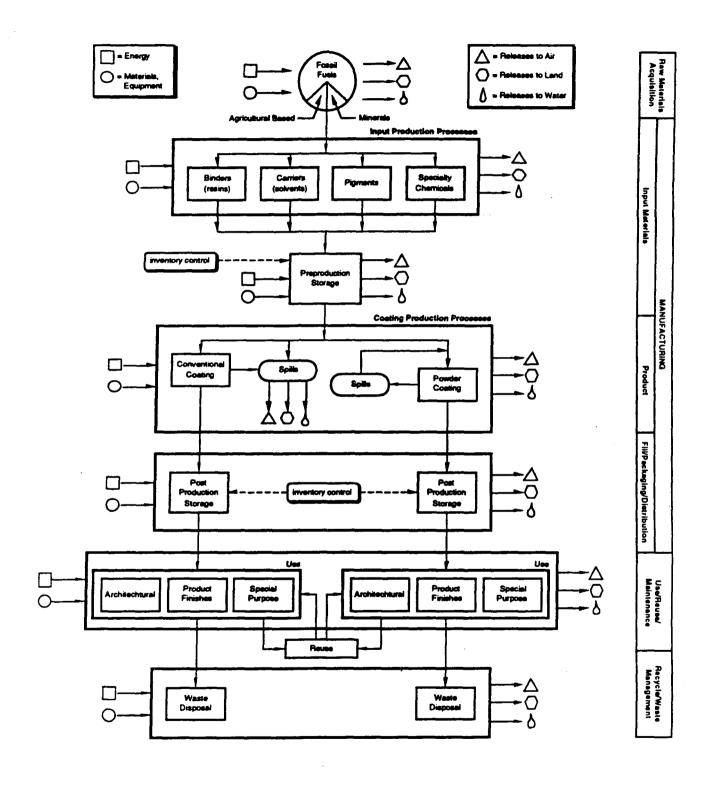


Figure 3. Basic Life Cycle System Boundaries for Coating Systems

TABLE 2. A TYPICAL CHECKLIST OF CRITERIA WITH WORKSHEET FOR PERFORMING A LIFE-CYCLE INVENTORY⁴

LIFE-CYCLE INVENTORY CHECKLIST INVENTORY OF:	
Purpose of Inventory: (check all that apply) Private Sector Use Internal Evaluation and Decision Making Comparison of Materials, Products, or Activities Resource Use and Release Comparison with Other Manufacturer's Data Personal Training for Product and Process Design Baseline Information for Full LCA External Evaluation and Decision Making Provide Information on Resource Use and Releases Substantiate Statements of Reductions in Resource Use and Releases	Public Sector Use Evaluation and Policy Making Support Information for Policy and Regulatory Evaluation Information Gap Identification Help Evaluate Statements of Reductions in Resource Use and Releases Public Education Develop Support Materials for Public Education Assist in Curriculum Design
Systems Analyzed List the product/process systems analyzed in this inventory:	
Key Assumptions: (list and describe)	
Define the Boundaries For each system analyzed, define the boundaries by life-cycle the system boundaries.	e stage, geographic scope, primary processes, and ancillary inputs included in
Postconsumer Solid Waste Management Options: Mark and desc Landfill Combustion Composting	
Basis for Comparison This is not a comparative study. State basis for comparison between systems: (Example: 1,000 unit products or processes are not normally used on a one-to-one basis.)	
Computational Model Construction System calculations are made using computer spreadsheets System calculations are made using another technique. Describe how inputs to and outputs from postconsumer solid was	
Quality Assurance: (state specific activities and initials of review Review performed on:	·
☐ Data Gathering Techniques ☐ Coproduct Allocation	Input Data
Peer Review: (state specific activities and initials of reviewer) Review performed on: Scope and Boundary Data Gathering Techniques Coproduct Altocation	Input Data Model Calculations and Formulas Results and Reporting
Results Presentation Methodology is fully described. Individual pollutants are reported. Emissions are reported as aggregated totals only. Explain why: in the report. List: Report is sufficiently detailed for its defined purpose.	Report may need more detail for additional use beyond defined purpose. Sensitivity analyses are included in the report. List: Sensitivity analyses have been performed but are not included in the report. List:

The type of data and level of specificity required is based on the previously defined goals, scope, boundary, and intended application of the inventory data.

One method to simplify the data gathering process is to break down the system at hand into a set of distinct subsystems. A "subsystem" is defined as an individual step or process that is part of the defined system. Each subsystem will have a distinct set of inputs and outputs that can be described in the inventory analysis. For example, although several components make up the life cycle of coating systems, the manufacturing stage of a particular coating might occur within a single facility. This single facility can be viewed as a subsystem (see Figure 4), so data can be gathered on all the manufacturing steps together. This example draws the subsystem boundary around the entire group of manufacturing steps within a given facility and not around each individual manufacturing step.

After identifying subsystem boundaries, the practitioner can collect the raw input and output data. To help manage potentially large amounts of data, the practitioner can organize the data into a chart or table like Table 3.

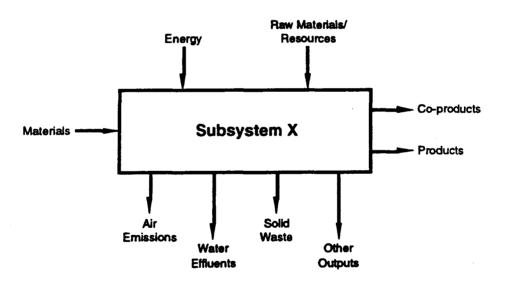


Figure 4. Generic Subsystem⁶

- 6.) Develop Stand-Alone Subsystem Data. To represent the inputs and outputs of the entire system, the practitioner must aggregate the individual subsystem data. Standalone subsystem data refers to standardized or normalized data that is amenable to aggregation with other subsystem data. The primary goals of developing stand alone data are the following:
 - To present data for each subsystem consistently by reporting the same product inputs and outputs from each subsystem.

TABLE 3. SUBSYSTEM WORKSHEET FOR MANAGING DATA⁴

LIFE-CYCLE INVENTORY CHECKLIST PART II - SUBSYSTEM WORKSHEET								
Inventory of:								
Life-Cycle Stage Desci	ription:	Quali	ty Assurance Approva	1:				
Date:	RIPTION:		· · · · · · · · · · · · · · · · · · ·					
	Data Value*	Туре⁵	Data ^c Age/Scope	Quality Measures				
SUBSYSTEM INPUTS								
Materials								
Process								
Other*								
Energy								
Process								
Pre combustion								
Water Usage								
Process								
Fuel-related								
	su	BSYSTEM OUTPUT	S					
Product								
Coproducts ¹								
Air Emissions								
Process								
Fuel-related								
Water Effiuents								
Process			`					
Fuel-related								
Solid Waste								
Process								
Fuel-related								
Capital Repl.								
Transportation								
Personnel				<u> </u>				

List measures of data quality available for the data item (e.g., accuracy, precision, representativeness, consistency-checked, other, or none).

Include nontraditional inputs (e.g., land use) when appropriate and necessary.

Include units.

Indicate whether data are actual measurements, engineering estimates, or theoretical or published values and whether the numbers are from a specific manufacturer or facility, or whether they represent industry-average values. List a specific source if pertinent (e.g., "obtained from Atlanta facility wastewater permit monitoring data").

Indicate whether emissions are all available, regulated only, or selected. Designate data as to geographic specificity, e.g., North America, and indicate the period covered (e.g., average of monthly for 1991).

¹ If coproduct allocation method was applied, indicate basis in quality measures column (e.g., weight).

• To develop the data in terms of the life cycle of only the product examined in the inventory analysis.

Two main activities need to be undertaken to achieve these goals. First, the practitioner must translate the input and output data from each subsystem to the same unit of production or time, as well as to the same unit of measure (e.g., pounds, tons, gallons). Second, the practitioner must identify and distinguish inputs and outputs attributable to the product in question from inputs and outputs attributable to the production of coproducts. Commonly called coproduct allocation, this process is usually based on relative weight.

7.) Construct a Computational Model. A computational model is needed that incorporates the normalized data and material flows into a computational framework using a computer spreadsheet or other accounting technique. The systems data that result from the model's computations will yield the total result for the inputs and outputs of the system in question.

The computational model uses "proportionality factors," which are quantitative relationships that reflect the relative contributions of the subsystems to the total system. For example, data gathered for manufacturing conventional coatings may have been based on 1,000 gallons of solvent. If the total system is based on 1,000 gallons of conventional coating (which is 70 percent solvents, 30 percent solids), the contribution of solvent to the total system is 0.70 times 1,000, or 700 gallons.

8.) Present the Results in a Transparent Manner. Transparency in this context refers to clearly communicating such aspects as the scope, system boundaries, data sources, methodologies used, limitations, and assumptions of the analysis. A tabular presentation format may best communicate results; however, the tables' format will vary between studies. Summary tables such as Tables 2 and 3 may be appropriate for illustrating results. In any case, the format for communicating life cycle inventory analysis results should be consistent with both the purpose of the inventory analysis and the goals and scope of the LCA in general.

Impact Assessment

Life cycle impact assessment is a systematic process, quantitative and/or qualitative, that identifies and describes potential environmental and human health impacts associated with the inputs and outputs of a given system. Although life cycle inventory analysis is well developed, life cycle impact assessment is in its infancy, so methodologies are either undeveloped or untried. Therefore, we only briefly describe this component.

To date, most LCAs have been strictly life cycle inventory analyses with no explicit impact assessment. These studies often implicitly interpret life cycle inventory results in a context that implies impacts. Failing to consider the methods used to evaluate and weight or rank the life cycle inventory items may convey that all inventory items have relatively similar impact potentials. Life cycle impact assessment makes explicit the methods used to assess the potential impacts resulting from a given system.

Life cycle impact assessment is fairly well developed on a conceptual level. A three-phase conceptual framework, developed by the Society of Environmental Toxicology and Chemistry (SETAC)⁵, has been used as a basis for developing life cycle impact assessment. A variation of these three phases contains the following activities:

- Classification: The process of assigning and initially aggregating life cycle inventory data to relatively homogeneous groupings of potential impacts of concern (e.g., photochemical smog, lung disease, fossil fuel depletion)—called assessment endpoints—within primary impact categories (natural environment, human health, and natural resources impacts).
- Characterization: Analyzing and possibly estimating the magnitude of
 potential impacts—called measurement endpoints—as actual or surrogate
 measures of assessment endpoints that were identified in the classification
 phase. Characterization involves using specific impact assessment tools known
 as conversion models and impact descriptors.
- Valuation: The explicit and collective process of assigning relative values and/or weights to potential impacts of concern (assessment endpoints) using formal valuation methods.

Figure 5 provides a conceptual schematic of these three stages. As illustrated in Figure 5, the sequence from the life cycle inventory to the improvement component is not necessarily linear, which is consistent with the three-component LCA triangle in Figure 1. The sequence involves interrelationships and feedback loops among the major components. For example, opportunities for environmental improvement can be realized at any phase of the LCA, but unplanned modifications may entail revisiting previously completed components.

Unlike other forms of impact assessment, life cycle impact assessment does not necessarily attempt to quantify actual impacts associated with a system. Instead, life cycle impact assessment attempts to establish a link between the inputs and outputs of a system and potential impacts. The ability to establish this link depends on the availability and use of specific impact assessment tools—called conversion models—to estimate the magnitude of the contribution of specific life cycle inventory items to potential impacts of concern (assessment endpoints).

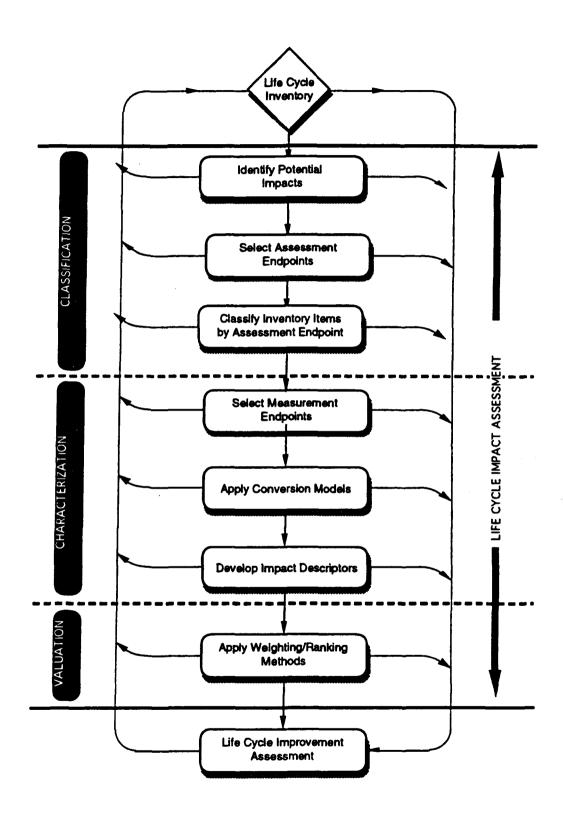


Figure 5. Life Cycle Impact Assessment Conceptual Framework

Recent forums (SETAC Life Cycle Impact Analysis Workshop in February 1992 and the SETAC Life Cycle Data Quality Workshop in October 1992) have identified a five-level tiered hierarchy of conversion models, shown in Figure 6.

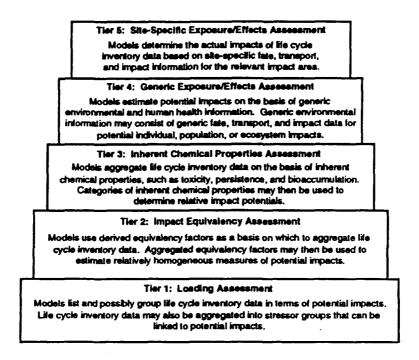


Figure 6. Five-Level Tiered Hierarchy of Conversion Models

One major constraint currently limits the applicability of conversion models—the lack of data on many environmental and human health effects. The general consensus is that the lack of this data limits practitioners to Tier 1- and Tier 2-type conversion models where impacts are not measured per se. Tiers 3 to 5 conversion models require more site-specific data as well as additional computational models. Gathering site-specific data and developing computational models are long-term goals.

Improvement Assessment

The improvement assessment component of LCA is a systematic process that identifies, evaluates, and implements opportunities for environmental improvements. Because the improvement component has not yet been developed or even discussed in a formal public forum, we do not discuss it in this paper. Preliminary discussions on improvement assessment have recognized that both quantitative and qualitative evaluations of improvement options may occur in this component. In assessing the two alternative coating systems, the improvement assessment component might recognize that the powder coating system not only eliminates VOC emissions but it also uses less energy and labor and produces less waste products. On a "less is better" basis, the powder coating system uses less inputs and generates less outputs; therefore, this system may be considered more

environmentally benign than the conventional coating system. In addition, the improvement assessment might also identify and implement opportunities to further reduce input use and output production within the powder coating system.

CONCLUSION

In an era of heightened awareness of environmental and human health effects resulting from products and processes, LCA represents an emerging tool for incorporating such concerns into decisionmaking processes. This paper outlines the LCA process, including goal definition and scoping, inventory analysis, impact assessment, and improvement assessment. Techniques used in this process could be applied to assess alternative coating systems to minimize potential impacts to the environment and/or human health.

Although much of LCA methodology remains to be developed, LCA currently may be used as both a screening tool for assessing potential environmental and human health impacts and a tool for making explicit those methods used to evaluate alternative coating systems that may have relatively similar or largely different components and/or effects.

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SESSION 2

TECHNOLOGIES

PAPERS PRESENTED:

"Radiation Curing Technology: Ultraviolet (UV) and Electron Beam (EB) Processing"

by

Richard W. Stowe

Fusion UV Curing Systems

Rockville, Maryland

"Environmental Compliant Thermoplastic Powder Coating"

by

David F. Ellicks

Department of the Air Force

Air Force Corrosion Program Office

Robins AFB, Georgia

"Supercritical Fluid Spray Application of Low-Pollution Coatings for Plastic Substrates"

by

Wayne Paul Miller

Kenneth A. Nielsen

Union Carbide Corporation

South Charleston, West Virginia

and

Tom Morrison

Red Spot Paint & Varnish Company, Inc.

Evansville, Indiana

"Utilizing Dispersion Resins with Inorganic Solids in a New Formulary Blending Process to Achieve Synergistic Results of Performance"

(Expanded abstract; paper not available.)

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Philip W. Coscia

Resources Conservatory International

Gustine, California

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

RADIATION CURING TECHNOLOGY Ultraviolet (UV) and Electron Beam (EB) Processing

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Radiation curing of polymeric materials is an efficient and relatively low temperature electricity-based technology with many applications in coating, printing, adhesives, electronics, and communication material. Radiation curing, which includes Ultraviolet Curing and Electron Beam technologies, can improve the overall physical or chemical properties of polymeric materials and produce superior results in bonding, surface finish, and durability to those of other technologies. Speed and controllability in these applications, suggest an increasing market for this electrotechnology in manufacturing worldwide.

BENEFITS

Both UV or EB Curing are highly desirable for processing, owing to benefits of productivity as well as advantages of being "clean" technologies. These radiation processes have a number of key attributes; they are:

- a solventless process -- cure is by polymerization rather than by evaporation, so VOC emissions are eliminated;
- a low temperature process -- heat is not required;
- a high speed process -- cure is nearly instantaneous;
- an energy-efficient process -- energy is invested only in the curing reaction, not in heating;
- easily controlled -- inks and coatings do not "dry," so do not set up in printing/coating equipment.

APPLICATIONS

Radiation-processing technologies offer several major advantages over other production methods. These benefits include rapid curing, low process temperatures, the absence of pollution, and substantially lower energy costs, as well as high-quality and specialized products. Typical product lines involve coatings (on wood, metal, paper, and plastic), inks (for letterpress, lithographic, gravure, and screen printing), and adhesives (for film, foil, or paper substrates). The industries using these technologies are diverse and varied; they include electronics, fiber optics, flooring, packaging, plastics, and printing.

MATERIALS

The essential ingredients of a radiation-curable material are:

- (1) Oligomers -- 30-90% concentration; completely reacted upon cure; primarily provide film properties such as flexibility, hardness, and chemical resistance; (equivalent to "resins" of conventional coatings) There are a number of choices of types which provide a variety of features and properties of the uncured and cured material, such as viscosity, cure speed, hardness, toughness, flexibility, weathering, etc.
- (2) Monomers -- 10-70% concentration; completely reacted upon cure; controls viscosity and polymer chain formation; (equivalent to "solvent" in conventional materials EXCEPT that it is completely reacted)
- (3) Photoinitiator (UV curing only) -- 1-5% concentration; a photo-active material which responds to (UV) light and initiates chain formation.
- (4) Additives and pigments -- conventional materials to alter stability, adhesion, tack, or appearance.

TECHNOLOGY: UV CURING

UV lamps are generally of two types: (1) Medium pressure mercury vapor arc lamps (usually called "arc lamps"), or (2) Medium pressure mercury vapor microwave-powered lamps (called "microwave powered lamps" or "electrodeless lamps").

The UV energy produced by the lamp bulb is focussed by a reflector onto a (moving) surface. The UV energy striking the surface causes the photoinitiator to trigger the polymerization reaction. The material is usually solidified ("dry") when it exits the cure zone.

Lamps are characterized by the UV light intensity at the work surface (irradiance), measured in Watts per square centimeter (W/cm²). Cure dose is a function of time (or process speed) and is measured in Joules per square centimeter (J/cm²). By using multiple lamps, the process width can be extended without limit.

A light enclosure is required to eliminate stray UV light and to provide protection to personnel from exposure to UV.

TECHNOLOGY: EB CURING

Electrons generated by a hot filament and cathode are accelerated by a high voltage to produce a flood of high energy electrons which are concentrated into a beam onto a (moving) surface. The energy of the electrons is a function of the accelerating voltage. Electron beam accelerators are characterized by their accelerating voltage: 300 kV or less is referred to as "low energy." Most curing accelerators are in this range. Process width is usually 130 inches or less.

Electrons striking and penetrating the uncured material cause a direct initiation of the cross-linking reaction in the material, and the material is immediately polymerized.

The dose (D), in megarads, received by a material is characterized by the electron current (I), the velocity of the process (S), and a factor (k) which is a function of the accelerator voltage, geometry, width and distance:

$$D(Mrad) = \frac{k \cdot I(mA)}{S(m/\min)}$$

The curing zone is surrounded by an enclosure to contain an inert (nitrogen) atmosphere. It is necessary to displace oxygen, which interferes with the curing reaction at the surface of high speed materials. Electrons striking oxygen molecules would also produce ozone. The enclosure is also shielded to prevent escape of radiation produced by the high energy electrons.

PRODUCT APPLICATIONS FOR UV PROCESSING

- Printing and Publishing
 - Book and magazine covers
 - Brochures and promotional materials
 - Compact disc boxes and album covers
 - Menus
- Consumer Products
 - Eyeqlass lenses
 - Trophies and plaques
 - Tape measures
- Wide web converting
 - Silicone release films
 - Vinyl flooring no-wax finish
 - Solar reflective films
 - Vinyl woodgrain laminating films

PRODUCT APPLICATIONS FOR UV PROCESSING (continued)

- Business Forms
 - Direct mail
 - Catalogs
 - Business forms
 - Sweepstakes mailings
- Narrow web converting
 - Labels and tags
 - Bar code printing
 - Lottery tickets
 - Stickers and decals
- Plastics
 - Headlamp lenses and bodies
 - Decorative caps and containers
 - Auto body moldings
- Medical devices
 - disposable syringes
 - Transdermal patches
 - Catheters
- Plastic container decoration
 - Shampoo and toiletry bottles
 - Toothpaste tubes
 - Styrofoam cups and containers
- Wood
 - Fillers and sealers for plywood and particle board
 - High gloss finishes on case goods
 - Wood flooring strips and parquet
- Electronics
 - Component marking
 - Conductive inks
 - Conformal coatings
- Metal Containers
 - Two piece (aluminum) beer and beverage cans
 - Three-piece (steel) cans and containers
 - Metal boxes
- Telecommunications
 - Optical fiber coatings
 - Printing on wire and cable insulation
 - Optical ribbons, cables and fiber coloring

PRODUCT APPLICATIONS FOR ELECTRON BEAM PROCESSING

Curing ("drying")

- Inks and coatings in offset lithography (e.g., printing folding cartons and flexible packaging)
- coatings on wood, Masonite or particle board to produce decorative panels
- Adhesives in laminating operations
- Silicone coatings on controlled- release products (e.g., label stock) and magnetic coatings on recording tapes and discs

Crosslinking

- Plastic films for high strength and temperature packaging materials (e.g., shrink wrap)
- Heat shrink tubing for electronic applications
- Wire/cable insulation to increase chemical resistance and allowable operating temperature

Sterilization

Medical products

Electron beam (EB) and Ultraviolet (UV) processing are sometimes considered to be competitive technologies, but in most cases, specific manufacturing requirements provide a clear differentiation between the two approaches, and they tend to be complementary. In some instances they may both be required.

RECYCLING OF RADIATION-CURED PRINTED MATERIAL

A study recently conducted by the Beloit Corporation, sponsored by RadTech International, found that all of the (UV/EB) ink/coating combinations were recyclable into board grades.

Furthermore, the study proved that for recycling into tissue grades, all materials require a system containing flotation while most also require centrifugal cleaners.

In addition, UV inks and sheetfed litho inks with waterbased coating also require dispersion, a common component in today's recycling mills, for recycling into tissue grades. For recycling into fine paper grades, most ink/coating combinations require dispersion and additional flotation.

Hence the Beloit study's conclusion: UV/EB printed and coated paper can be recycled into tissue and/or paper grades using commercially available equipment. In fact, UV/EB cured paper is just as recyclable as other materials.

UV and EB MARKETS

U.S. Market for Radiation Curable Coatings, Inks and Adhesives, by End-user Industry (Value \$mm)

Industry	1991	1996	t Change
Electrical / Electronics	74	140	90%
Packaging	67	103	54%
Graphic Arts	31	49	58%
Wood furniture & Construction	49	69	41%
Automotive	8.4	12.7	51%

Source: Frost and Sullivan, Inc. - 1992

RECENT TREND AND SHARE

Annual Coatings Market Survey (percent of total volume)

TYPE OF COATING USED	1989	1990	1991	1992
Conventional	47.8	46.0	41.6	32.5
High-solids	14.9	16.5	16.4	16.3
Two-component	12.2	12.9	11.6	11.5
Powder	11.1	11.5	12.8	16.7
Waterborne	9.1	11.2	11.8	16.9
Vapor-cure	1.6	.7	1.4	1.1
Radiation-cure	1.4	. 9	2.0	2.3
Other	1.9	3.3	2.5	2.5

Source: Industrial Finishing - January 1992

"Radcure coatings today comprise about 3% (\$300 million) of the U.S. industrial coating market (\$10 billion). Indeed, UV and EB coatings that cure instantly, rapidly and with minimal VOC certainly have a bright future. The share could reach 10% (\$1 billion) by 2000".

Source: Industrial Finishing - May, 1992

CONCLUSION

Radiation-processing technologies offer several major advantages over other production methods. These benefits include rapid curing, low process temperatures, the absence of pollution, and substantially lower energy costs, as well as high-quality and specialized products. Typical product lines involve coatings (on wood, metal, paper, and plastic), inks (for letterpress, lithographic, gravure, and screen printing), and adhesives (for film, foil, or paper substrates). The industries using these technologies are diverse and varied; they include electronics, fiber optics, flooring, packaging, plastics, and printing. While still minor manufacturing techniques, their industrial use is expected to expand greatly, with a continued annual growth of 15 to 20%.

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(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

ENVIRONMENTAL COMPLIANT THERMOPLASTIC POWDER COATING

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INTRODUCTION

In the early 1970s, inhibited epoxy primer and aliphatic polyurethane paint systems were applied to a majority of Air Force weapon systems. coating effectively reduced the level of corrosion on the exterior surfaces of aircraft. This resulted from "built-in" corrosion inhibitors and the coating's capacity to bend without cracking as the surfaces of the aircraft flexed during flight. The Air Force recognized the 1980's as the decade of environmental awareness. The 1990's, on the other hand, will introduce the new technologies required to fully address all the environmental considerations. The current painting operations generate carcinogenic substances (methylene diisocyanates), air pollution (volatile organic compounds from solvent-borne coatings), and hazardous wastes (paint waste containing strontium, barium, or zinc chromates and cadmium). Historically, the Air Force has used primers and topcoats because of the excellent corrosion The Air Force, in general, and Warner Robins Air protection they provide. Logistics Center, in particular, have been striving toward the elimination of The goal is for the isocynates, volatile organic compounds, and heavy metals. paint operation to conform to the increasingly stricter environmental and health requirements. The painting operation requires very expensive facilities (explosion proof lighting and fixtures, drainage system, and one pass heating/cooling ventilation systems), hazardous waste disposal facilities, air supplied respirator devices, medical examinations, and extensive training. In addition, special high volume/low pressure paint spraying equipment and high solids solvent-borne coating systems are being used to help reduce volatile organic compounds.

In order to reduce the environmental/health hazards and the cost of disposing of the hazardous waste, the Air Force Corrosion Program Office continually evaluates potential new coatings and application techniques. One new and promising coating and application technique is Thermoplastic Powder Coating (TPC) applied through flame spraying equipment. This paper describes the Air Force Corrosion Program Office's initial evaluation, economic analysis, environmental analysis, and the preliminary results from applications testing done at Warner Robins Air Logistics Center, Robins Air Force Base, Georgia.

BACKGROUND

There has been a long-term problem at many Air Force bases with the use of hazardous coatings/coatings removal materials and the lack of adequate facilities for performing corrosion prevention and control processes on nonpowered aerospace ground equipment, munitions handling equipment, nonfueled industrial vehicles, trailers, containers, components, and civil engineering real property facilities/structures. Standard coatings are not meeting the durability and maintainability requirements of the units and pose a hazard both to the health of personnel and the environment. Lack of authorized and available corrosion facilities in the munitions or aerospace ground support equipment organizational units for depainting/repainting of the end items and parts is a problem at many bases. Keeping this in mind, the Air Force Corrosion Program Office is always looking for new technologies to protect Air Force assets from corrosion damage. We are also mindful that the life cycle environmental considerations must be integrated into product/process engineering design procedures.

THERMOPLASTIC POWDER COATING AND APPLICATION EQUIPMENT SYSTEM DEFINITION AND EVALUATION

System Definition

Currently, there are three common techniques for applying powder coatings: electrostatic deposition, fluidized bed dipping and flame spraying. Electrostatic deposition is accomplished by immersing an electrically grounded part in a fog of powder sprayed from an application gun which transfers a static charge to the powder. The powder is attracted to the part and clings to the surface. The coated part is then heated (oven or infrared lamps) to bake and fuse the coating to the part. Fluidized bed coating involves dipping preheated parts into a column of powder which has been fluidized (agitated) by passing air up through the column. The heat retained by the part serves to melt and fuse the coating. In flame spraying, powder is blown through a flame, melted, and directed onto the material being coated.

The TPC and application equipment system is similar to metal flame spraying equipment with thermoplastic or thermoset powder replacing the metal powder. Some of this equipment is expensive and too complicated to use at field-level bases. The coating process is simple. In general, the bare metal surface to be coated is first inspected for cleaniness (oils, hydraulic fluids, etc.) and then preheated to approximately 175 degrees Fahrenheit with the application flame gun or nozzle to drive off moisture and to ensure that the applied plastic will flow smoothly. The preheating step is followed by application of the finely ground, pigmented polymer to the desired thickness either as solid or molten powder. The final step is the continued heating of the applied polymer to insure proper flow-out to the optimum coating temperature range of 320 to 425 degrees Fahrenheit, as monitored by a hand-held infrared pyrometer. After the coating cools, the painting operation is complete. For the thermoplastic powders, no chemical reaction or change in the molecular structure occurs during the coating process. Therefore, these coatings have the potential for easy repair if damaged by simply reheating or re-applying additional powder. The coating is soft, one coat, glossy, thick (10-12 mils), durable, easy to apply, repairable, safe for workers, and environmentally compliant.

The thermoplastic powder is generated by grinding polymer pellets at cryogenic temperatures using liquid nitrogen as a refrigerant. Originally, Envelon powder was supplied directly by Dow Chemical Corporation; however, Dow has now licensed that process to Morton, International, a major commercial supplier of industrial powder coating materials. Plastic Flamecoat Systems (PFS) of Houston, Texas (an alternate TPC equipment manufacturer) grinds DuPont Nucrel and is currently the only source for this powder. The Dow/Morton product is a "melt blend" material in which pigments, UV stabilizers, and other additives are blended with melted polymer before grinding. The DuPont/PFS powder is "dry blended" by mixing additives with the powder after grinding. Both powders cost relatively more than the convential solvent-borne coating systems. Both materials are considered "environmentally compliant" by current EPA federal and state regulations.

Both the Dow and DuPont powders may be obtained in a range of "melt index" values. Low melt index polymers are more viscous at any given

temperature than are high melt index polymers. In general, the low melt index powders yield tougher coatings but are more difficult to apply because they require higher temperatures to achieve flow-out during application. Both polymers melt at about 300 degrees Fahrenheit and flow over a substrate that has been preheated to a temperature of 150 to 175 degrees Fahrenheit. If coating temperature exceeds 425 degrees Fahrenheit for extended periods of time (minutes), significant polymer chain cross-linking occurs, and the coating effectively converts from a thermoplastic to a thermoset material. When this happens, field repairability of the coating by reheating is lost. If coating temperatures exceed 650 degrees Fahrenheit during application, the polymer is permanently damaged and the coating is destroyed. To avoid overheating, the coating temperature is carefully monitored by the applicator with a hand-held infrared pyrometer.

System Evaluation

A TPC application system was selected by the Air Force for a field-level test program. This system was chosen as the most suitable for evaluating the current state of flame coating technology and its potential for an alternate to conventional solvent-borne paint systems. The simplest and most commonly used TPC flame spray application systems are entirely pneumatic. These systems require only clean, dry compressed air and fuel (typically liquid propane) for operation. Powder is stored in a hopper and delivered by hose to the gun in a stream of compressed air that transports powder from the hopper with a venturi. Propane is delivered to the gun through a separate hose and mixed with air at the gun exit where it is ignited. The equipment operator sets the air, powder, and fuel flow rates with controls located on or near the gun. The powder/air mixture blows through the flame, melts and flows onto the surface to be coated.

Dow and DuPont are the two major domestic suppliers of thermoplastic polymer resins developed for flame spray application. Each manufactures a similar commercial thermoplastic resin. Dow "Envelon" is an Ethylene Acrylic Acid (EAA) copolymer. DuPont "Nucrel" is an Ethylene Methacrylic Acid (EMAA) copolymer. These copolymer formulations were developed to enhance polyethylene coating adhesion. Dow and DuPont have worked closely with application equipment manufacturers to develop effective TPC flame spraying systems. Some equipment suppliers restrict the use of their hardware to specific polymers. The flame spraying equipment manufactured by American Thermoplastics, Inc. (AT) of Mesa, Arizona, has been selected for field-level evaluation at several Air Force bases. AT allows the use of all commercially available TPC materials; however, the use of Dow Envelon is recommended. Dow materials were used in this test program.

System Characteristics and Modifications

Of the three flame spraying systems evaluated, the UTP system had the most sophisticated flame application hardware. UTP uses an electro-pneumatic system requiring oxygen as well as compressed air and propane. This method provides a smaller, hotter flame yielding better temperature control and better flowout of thermoplastic powder. This has lead to the current development effort focused upon improving flow-out temperature and the spray pattern. The Air Force is looking at modifying the nozzle to use a premixed combustion instead of a diffusion flame for better heating control. In

addition, we are seeking modification of the nozzle to change from a circular to a tapered oval spray pattern to widen the pattern and to improve the coating uniformity (thickness variations).

Further nozzle development may also be necessary for coating hard-to-reach areas, e.g., angles, tubing, and grating, found on maintenance stands or other complex equipment residing in the Air Force inventory.

Thermoplastic powder coatings have notable performance properties that address the environmental/health problems inherent with standard Air Force polyurethane coating systems. For example, these coatings exhibit excellent resistance to various chemicals, solvents, and reagents. This coating should not be used in contact with chlorinated solvents, fuming or strong oxidizing acids, aromatic alcohols, or heterocyclic aldehydes. These coatings have shown excellent abrasion resistance and good barrier qualities to prevent corrosion, and they are environmentally compliant. These coatings have the ability to be applied in almost all types of weather in any area, inside or outside, where it is safe to use a flame. The thermal spray coatings are proving useful in many Air Force applications. They are not appropriate for every application. This process does have drawbacks such as incompatibility with live munitions or combustibles, problems with thin metal and composites, slow application rate (50 to 100 square feet per hour), high substrate temperature effecting the heat treatment of alloys, and high material cost. This information is based on the preliminary laboratory testing using the test requirements in MIL-C-83286 as a comparison and guide to base our above conclusions.

Continuing Efforts

Warner Robins Air Logistics Center is pursuing an aggressive program to test and evaluate thermoplastic powder coating flame spray application methods with the desire to implement this technology as one of the new alternatives to solvent-borne coatings. Current efforts involve optimizing the spray nozzle for better coating applications and developing flameless techniques for coating with thermoplastic/thermoset powders. The Air Force Corrosion Program Office will continue to strive to identify a coating system that will provide corrosion protection while eliminating environmental/health problems throughout the Air Force.

Conclusions

Thermoplastic powder coating flame spray application methods produce a simple, highly reliable, safe, environmentally compliant, single coat capability to augment the standard Air Force epoxy-polyurethane coating systems. TPC will also eliminate some requirements for several current maintenance operations, e.g., chemical conversion coatings, long paint drying times, air supply respirators, and expensive facilities. The need to convert from standard coating to thermoplastic/thermoset powder coatings is being driven by the requirement to reduce hazardous wastes, enhance personnel safety, provide a cleaner environment, and minimize coating facilities.

AR FORCE

CORROSION PROGRAM

THERMOPLASTIC POWDER COATINGS (TPC)

Briefer:

DAVID F. ELLICKS

Materials/Mechanical Engineer Air Force Corrosion Program Office

in: AFCiille

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Briefing in: afcorr

OBJECTIVE

OBJECTIVE

EVALUATE THE FLAME SPRAYED TPC
TECHNOLOGY AS AN ALTERNATIVE
TO STANDARD AIR FORCE EPOXY/
POLYURETHANE COATING SYSTEM

POLYETHYLENE PLASTIC

-ETHYLENE ACRYLIC ACID COPOLYMER (DOW) (MORTON)

-ETHYLENE METHACRYLIC ACID COPOLYMER (DUPONT)

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APPROACH

APPROACH

ENGINEERING STUDY--STARTED 1 OCT 91 CONTRACTOR: SCIENCE APPLICATIONS INTERNATIONAL CORPORATION (SAIC) THREE PHASES:

- * PHASE I INDUSTRY SURVEY/SITE VISITS
- * PHASE II EQUIPMENT/COATINGS EVALUATION
- * PHASE III EQUIPMENT/COATINGS FIELD TESTS

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APPLICATION

EQUIPMENT APPLICATION

NONPOWERED AEROSPACE GROUND EQUIPMENT
MUNITIONS HANDLING EQUIPMENT
NONFUELED INDUSTRIAL VEHICLES
TRAILERS
COMPONENTS

9

CORROSION PROGRAM

POTENTIAL BENEFITS

ONE COAT

NO/LOW VOLATILE ORGANIC COMPOUNDS (VOCs)

NO TOXIC FUMES

NO HAZARDOUS WASTE

FIELD APPLIED/REPAIRABLE COATING

EXTENDED SHELF LIFE

REDUCE VENTILATION/FACILITIES REQUIRED

NO CURE TIME - COOLING TIME

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DRAWBACKS

DRAWBACKS

NO CORROSION INHIBITORS
THICK
ORANGE PEEL APPEARANCE
SLOW COATING RATE
LIMITED USE

HIGH TEMPERATURE DEGRADATION

ROUND SPRAY PATTERN (NOT OVAL)

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PROCEDURE

TPC APPLICATION PROCEDURES

PREPARE SURFACE TO BARE METAL

INSPECT FOR CLEANINESS

PREHEAT SURFACE TO 150 - 170 DEGREES F

START APPLYING TPC

INSURE PROPER FLOW-OUT TEMPERTURE (350-400 DEGREES F)

- USING HAND-HELD INFRARED PYROMETER

AFTER COATING COOLS, ITEM READY TO USE

N

TEST SITES

FIELD EVALUATION SITES

EGLIN AFB FLORIDA

ANDERSEN AFB GUAM

KADENA AFB JAPAN

ELEMENDORF AFB AK

ω

AR FORCE CORROSION PROGRAM

PRESENT STATUS

STATUS

PHASE II

MID AUG 93

PHASE III

DEC 93

PHASE IV

DEC 94

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SUPERCRITICAL FLUID SPRAY APPLICATION OF LOW-POLLUTION COATINGS FOR PLASTIC SUBSTRATES

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INTRODUCTION

Increasing pressure from groups concerned about the fate of the environment have helped spawn a new generation of heightened governmental regulation designed to significantly reduce the amounts of volatile organic compounds (VOC) emitted. The coatings industry has been the target of many of these regulations. As a result, coatings formulators and applicators have had to develop new methods or products to remain compliant. Very often the resulting coatings have been dramatically inferior to their conventional organic solvent-borne precursors in terms of economics, appearance, performance, and convenience.

Two strategies are prevalent today in reducing the amount of organic solvent emissions from coatings. The first, removing the organic solvent from the coating prior to the application, is the most widely practiced. The second, removing the solvent from the air handling system after it has been released from the coating and prior to release to the outside atmosphere, is less widely practiced because of the high capital and operating costs involved, and the intimidating level of sophistication. It is also inappropriate in those states that regulate emissions based on the applied VOC level. Additionally, with the fuel tax strategy proposed by the current administration, fuel-intensive systems, such as incinerators, are less attractive.

Removing the solvents prior to the application typically results in viscosity increases in the coating. The increased viscosity of the coating has dramatically detrimental effects on the processability, sprayability, and appearance of the coating. To overcome this, formulators have frequently resorted to reducing the molecular weight of the base resin(s) in the coating in order to keep the viscosity of the coating low enough to handle. This approach has typically been referred to as high-solids coatings.

Typically, reactive coatings have suffered less from the high-solids approach than have conventional lacquer coatings. This has been because the reactive functionality of the base resin

time required, are costly, and therefore unattractive to many applicators and formulators.

In spite of the many advantages that solvent-borne coatings have, they are typically characterized by high emissions of volatile organic compounds, and consequently are under increasing regulatory scrutiny. The development and introduction of the supercritical fluid spray process has not only allowed this challenge to be overcome, but also allowed for further performance and economical improvements in solvent-borne coatings for plastics.

SUPERCRITICAL CARBON DIOXIDE AS A COATING SOLVENT

Supercritical fluids are interesting and useful because they have properties that are intermediate to both gasses and liquids. Because of the high temperatures required to drive normal liquids into the supercritical regime, compressed gasses are the most widely utilized supercritical fluids. Supercritical fluids have become increasingly more widely used in a variety of industrial applications within the last dozen years. Thorough treatments of the properties and uses of supercritical fluids are provided by Johnston (1) and McHugh and Krukonis (2).

Perhaps the most important property of supercritical fluids is the relationship between density, and hence solubility, and pressure, and not just temperature. Because supercritical fluids are highly compressible in nature, significant changes in density (and solubility) can be initiated with relatively small changes in pressure. Supercritical fluids have lower densities, higher rate of diffusion, lower viscosities, and higher penetration ability when compared to normal liquid organic solvents. These properties permit supercritical fluids to penetrate polymer systems and then mix and equilibrate faster than normal solvents.

Supercritical carbon dioxide is the primary, but not only, supercritical fluid utilized in the supercritical fluid spray process. Along with the attributes that supercritical carbon dioxide shares with other supercritical fluids, it has many other significant attributes for use in coatings applications.

- 1) The critical conditions of carbon dioxide (31 degrees Celsius/88 degrees Fahrenheit, 1070 psi) are easy to obtain. The critical temperature is only slightly above room temperature, and the critical pressure is well within the designed containment pressure of typical airless spray equipment.
- Carbon dioxide is much less toxic than normal organic solvents. It has a high threshold limit value (TLV) of 5000 parts per million (0.5%). The health effects of carbon dioxide are slight, when compared to other liquid organic solvents. The concentration of carbon dioxide observed in the spray booth has been observed to be innocuous in the range of normal spray operation.
- Carbon dioxide is non-flammable and mostly inert. Also, the supercritical fluid compatible coating has a much higher flash point because it has less solvent. This helps reduce the overall flammability in and around the spray booth and spray line. Along with the safety benefits of a less flammable area, it can also be less expensive for insurance purposes.
- 4) Supercritical carbon dioxide, because of its small molecular size and high solubility, can easily penetrate most polymer systems to significantly improve the viscosity of most coating formulations.

- Carbon dioxide is a low cost commodity chemical that is readily available throughout the world. It is available in a number of packaging configurations designed to meet the supply needs of both large- and small-volume coating applicators. Bulk prices of carbon dioxide are currently less than ten cents per pound in most parts of the country.
- 6) Carbon dioxide is not considered to be a volatile organic compound by any of the state or federal regulatory agencies.

REDUCTION OF THE "GREEN HOUSE" EFFECT

The release of carbon dioxide from coatings formulated for spraying with supercritical fluids, when considered by itself, has little or no effect on local or global environments. For example, an automotive plant that sprays a top coat on 250,000 automobiles per year would emit less carbon dioxide than is emitted by soft drinks in the United States in just eight hours. In fact, utilizing carbon dioxide as a coating solvent actually reduces the amount of "green house" carbon dioxide that is generated during coating operations.

- The supercritical fluid spray process uses carbon dioxide created as a byproduct from natural gas wells, fermentation plants, ammonia plants, and other industrial applications, which would be released anyway. Therefore, no new carbon dioxide is created by the process.
- In general, one pound of carbon dioxide is used to replace one pound (or more) of normal organic solvents in the supercritical fluid spray process. When that one pound of normal organic solvent is emitted to the atmosphere, it eventually oxidizes to produce 2.3 to 3.3 pounds of new carbon dioxide. The one pound of byproduct carbon dioxide from the supercritical fluid compatible coating system can not further oxidize to produce any additional carbon dioxide.
- The high volumes of air from the booths produce a low solvent concentration in the conventional application. Therefore, thermal oxidation abatement requires the burning of substantial amounts of fuel. In one automotive paint operation studied, thermal oxidation abatement produces 18 pounds of new carbon dioxide per pound of organic solvent.

The amount of recycled carbon dioxide, if used to apply coatings, would certainly be dwarfed by emissions from other sources. In fact, the total amount of recycled carbon dioxide utilized industrially in the United States is less than one-third of one percent of the carbon dioxide generated from coal burning for power plants; oil and natural gas for home heating; automotive fuels; and from the food industry.

SPRAY GENERATION AND CONDITIONS

The supercritical fluid spray process uses commercial spray equipment specifically designed and manufactured by the Nordson Corporation, of Amherst, OH, to be compatible with the coating materials and the properties of supercritical fluids. The supercritical pressures are well within the

standard regime of airless spray, allowing the use of airless spray guns, spray nozzles, hoses, and pumps. The supercritical temperatures are well within the regime of conventional heated paint systems. Because there is not a need for any exotic spray equipment, a wide selection of previously developed accessories for other paint systems can be utilized.

In order for the carbon dioxide, which is a gas under normal conditions, to be mixed with the coating formulation, it is necessary to pressurize the mixture to maintain the supercritical conditions necessary to achieve the optimum benefits.

The amount of dissolved supercritical carbon dioxide used to spray any given coating formulation is a complex function of the solids level, solubility, viscosity characteristics, pigment loading, and the desired spray pressures and temperatures. Another unique feature of the supercritical fluid spray process is that the carbon dioxide level in the coating can be used to regulate the film build, and, to some extent, the dry time of a coating. When spraying at constant pressure through any given nozzle of fixed flow, as the amount of carbon dioxide increases, the amount of coating material decreases. Thus, increasing the concentration of carbon dioxide reduces the deposited film thickness. As the film thickness decreases, so does its dry time. When the film thickness is held constant, usually by reducing the application rate (traverse speed), the dry time is also decreased somewhat from the increased loss of solvent in the spray fan. The typical application range is from 10 to 50 weight percent carbon dioxide, and the mixture of carbon dioxide and coating material is usually sprayed as a single-phase solution.

In order to make the carbon dioxide supercritical, and offset the cooling that occurs as the carbon dioxide diffuses from the solution and expands as a free gas in the spray, the solution is heated. Because carbon dioxide solubility is inversely proportional to temperature, and viscosity is directly proportional to temperature, an optimum spray temperature can exist. The typical range is from 40 to 70 degrees Celsius (100 to 160 degrees Fahrenheit).

The dissolved carbon dioxide usually reduces the spray viscosity to less than 50 centipoise. The coating material usually has a formulated viscosity of from 500 to 3000 centipoise, but materials with much higher viscosities have been successfully sprayed. The amount of viscosity reduction is a function of the polymer system, carbon dioxide concentration, temperature, pressure, and solubility. The viscosity reduction is important because it allows the spray solution to be readily atomized into a series of fine droplets necessary to deposit a high quality, uniform, film of coating material.

SPRAY CHARACTERISTICS

Supercritical carbon dioxide functions both as a viscosity reducer and a generator of vigorous atomization. This vigorous atomization is produced by a new mechanism that remedies the defects of airless spraying and produces a high quality, uniform, film.

Conventional airless spray techniques are often characterized by coarse atomization and defective spray fans that limit their usefulness to the application of low-quality films. The atomization mechanism employs a high pressure drop across the spray orifice to generate a high velocity liquid film. The film typically becomes unstable when the induced shear generated from the high velocity differential from the film to the surrounding air exceeds the surface tension and cohesive forces in the film. When the shear is high enough, the film disintegrates in a series of filaments and droplets. Because the surface tension and cohesive forces in the film are not completely overcome, the resulting spray consists of non-uniform size droplets and filaments. The spray fans resulting from this

mechanism of atomization tend to contain jets that limit the ability to deposit a high quality, uniform film.

Supercritical fluid sprays using carbon dioxide have a significantly different atomization mechanism. The resulting spray is airless in nature, but has all of the desirable traits of the air spray, but without the high air volumes. A feathered spray, with the spatial uniformity of fine droplet sizes necessary for obtaining high quality films and high transfer efficiencies, is produced from the vigorous decompressive atomization provided by the supercritical carbon dioxide.

The vigorous decompressive atomization is believed to be produced when the dissolved supercritical carbon dioxide in the spray solution suddenly becomes exceedingly supersaturated as the spray exits the nozzle and undergoes a rapid and large pressure drop. The dissolved carbon dioxide is driven forcefully to the gaseous state. The rapid gasification of the carbon dioxide overwhelms the surface tension and cohesive forces of the spray solution before an extensive liquid film can form at the nozzle. By disrupting the formation of the liquid film, the defects of the airless film are avoided. Because the fan is no longer constrained by the surface tension and cohesive forces of the airless fan, a wider fan can be generated at the nozzle exit. This permits the formation of a rounded parabolic-shaped spray fan with high uniformity of droplet sizes. The fan is characterized by tapered edges similar to those of conventional air spray fans. The tapered edges permit the coating material to be deposited uniformly in a wide central region, with progressively less coating deposited towards the edges of the fan. This is particularly desirable when there is a need to overlap adjacent layers of sprayed coating to produce a uniform film thickness. Fan widths of the spray are regulated by nozzle selection, as is done with conventional airless spray.

Laser light scattering analysis has shown that the typical supercritical fluid spray fan has atomized droplets that range in size from 20 to 50 microns. This is dramatically smaller than the coarser atomization (70 to 150 microns) measured for normal airless spray fans.

Additionally, the decompressively atomized droplets decelerate rapidly after exiting the spray nozzle to provide a soft spray with low deposition velocities. The shear induced by the decompressive atomization, which causes the droplets to leave the nozzle at wide angles to make the parabolic fan, creates a large braking force to the droplet. Additionally, much of the droplets momentum is dissipated by the diffusion of carbon dioxide. One acrylic coating was measured to have a superficial spray velocity of 82 meters per second (266 feet per second) at the nozzle. At typical spray distances of 30 to 40 centimeters (11.75 to 15.75 inches), the average velocity had dropped to seven meters per second (23 feet per second). The maximum droplet velocity is only 10 meters per second (33 feet per second).

Additional evidence of the rapid release of the carbon dioxide can be found by observing the rapid cooling of the heated spray that occurs at very short distances from the spray nozzle. The cooling of the decompressively atomized spray occurs much faster than the cooling of conventional heated sprays. A conventional airless spray, heated to 60 degree Celsius (140 degrees Fahrenheit), does not cool back to ambient temperature until it is almost eight inches from the nozzle. The decompressively atomized spray, heated to the same temperature, reaches ambient temperature within less than one inch of the nozzle. This rapid cooling is important because it reduces the amount of solvent that evaporates from the spray, permits more efficient solvent use, and reduces exposure of workers in the spray area to solvent vapors.

TRANSFER EFFICIENCY

In order for the full benefits of VOC reduction to be realized, it is also necessary to achieve high transfer efficiencies. Because transfer efficiency depends on a large number of variables relevant to the application for which it is measured, it is not possible to compare the efficiencies of one application to those of another. In order to obtain meaningful values, it is necessary to measure efficiencies in situ. It is also easy to be mislead if maximum values of one application method are compared to those of another if the quality of the applied film on the part is disregarded. For example, larger droplet sizes are easier to deposit than smaller droplet sizes, but typically provide a lower quality film.

Both independent laboratory testing and commercial production performance measurements have demonstrated that the supercritical fluid spray process can provide improved coating appearance and performance without sacrificing material utilization, which has been the traditional trait of previous spray processes designed to reduce volatile emission.

One of the major spray equipment companies made a thorough examination of the transfer efficiencies of the supercritical fluid spray process. The test procedure that they utilized involved spraying spaced panel targets on a conveyor line. The results showed that the supercritical spray process provided significantly superior transfer efficiency when compared to air spray systems. The transfer efficiencies of the air-assisted airless spray system and the supercritical fluid spray process, at spray pressures of 1200 to 1500 psi, were not dramatically different. In another test, the transfer efficiency of the decompressive spray was measured by foiling an entire automobile body and spraying it using the supercritical fluid spray process. The overall transfer efficiency measured in the test was eighty percent.

In addition to measuring transfer efficiencies, it is useful to consider the amount of coating solids used per part sprayed. In another study, the supercritical fluid spray process was compared to a high-volume, low pressure (HVLP) spray system. The conventional formulation was sprayed at nineteen weight percent solids. The coating formulated for use with the supercritical fluid spray process contained forty-two weight percent solids, which yielded a sixty-seven percent solvent reduction from the conventional formulation. Transfer efficiencies were measured by spraying a series of flat parts 20 x 16 inches in size. The transfer efficiency of the supercritical fluid spray process was measured to be five to eight percentage points lower than for the HVLP spray because of the smaller droplet size. However, comparison of the production sprays showed that the parts sprayed with the supercritical fluid spray process demonstrated an improved coating appearance with thinner film builds. This resulted in an overall twenty-seven percent reduction in coating solids usage, and a realized solvent usage reduction of seventy-six percent when compared to the HVLP spray system.

At one commercial installation of the supercritical fluid spray process, the amount of solvent used per part sprayed is sixty percent less than was experienced prior to conversion of the spray line from the air-assisted airless spray process. This solvent reduction is only slightly less than the solvent reduction in the reformulated coating. However, the parts sprayed by the supercritical fluid spray process have a superior appearance to those sprayed by air-assisted airless spray. Additionally, higher film builds, without runs or sags, are possible on vertical surfaces using the supercritical fluid spray process. The higher achievable film builds contribute to the improved appearance in this application, and, combined with the improved appearance, permit a reduction in number of production steps necessary.

At another commercial installation of the supercritical fluid spray process, the reformulated coating has sixty-seven percent less solvent than the conventional formulation applied by air-assisted airless spray guns. In this application, the supercritical fluid spray process enables the same coating appearance to be achieved at lower film builds. Overall coating solids usage has been reduced by forty percent, allowing an overall solvent usage reduction of eighty percent.

COMPARATIVE VOC, COVERAGE, AND COST DATA FOR PLASTIC COATING

Red Spot Paint, a licensee of the supercritical fluid spray process, has developed several coatings for use with the process. In doing so, it was important for them, and ultimately their customers, to understand both the technical and economic aspects of the technology. Extensive comparative data, in terms of VOC, coverage, and cost, has been generated and compiled.

In comparing a conventional automotive-quality exterior acrylic lacquer to the version of the coating reformulated for use in the supercritical fluid spray process, it was immediately apparent that a VOC reduction, to the compliant level, was achieved. Michigan Rule 632, the applicable regulation determining compliance, requires that the coating be applied at less than 5.0 pounds per gallon of VOC. In addition to the VOC reduction obtained, all of the air toxics, as regulated by the Clean Air Act, were eliminated from supercritical fluid spray coating formulation.

	CONVENTIONAL	SUPERCRITICAL FLUID
	FORMULATION	FORMULATION
WEIGHT SOLIDS (supplied)	25%	. 36%
WEIGHT per GALLON (coating)	7.50 pounds	7.77 pounds
VOC (supplied)	5.62 lb/gal	4.97 lb/gal
SOLVENT REDUCTION	100%	NONE
WEIGHT per GALLON (reducer)	6.68 lb/gal	NONE
VOC (applied)	6.24 lb/gal	4.97 lb/gal
MI Rule 632 COMPLIANT?	NO	YES

Initial comparison of the VOC data does not make the supercritical fluid spray formulation seem too impressive. Relatively, speaking, 4.97 pounds per gallon of VOC does not seem to be a large improvement over 6.24 pounds per gallon of VOC. However, when the coverages (calculated for 1.0 mil dry film thickness with 100% transfer efficiency) of the two coating formulations are compared, the advantages of the supercritical fluid spray formulation become much more dramatic.

	CONVENTIONAL FORMULATION	SUPERCRITICAL FLUID FORMULATION
VOLUME SOLIDS (supplied)	18.9%	28.0%
Theoretical COVERAGE (supplied)	303 ft ² /gal	449 ft ² /gal
SOLVENT REDUCTION	100%	NONE
VOLUME SOLIDS (applied)	9.45%	28.0%
Theoretical COVERAGE (applied)	152 ft ² /gal	449 ft ² /gal

The parameter that stands out the most in the above data is the theoretical coverage data of the conventional solvent-reduced coating. The applied coverage of the supercritical fluid formulation is almost three times that of the conventional formulation. The seemingly small difference in the VOC belies the fact that there is actually a huge difference in the coverages of the two formulations.

While improvements in VOC and coverage are important, it has long been understood that the best way to improve a paint is to reduce its cost. Without a financial payback, many applicators are unwilling to implement VOC reducing technologies unless forced to by federal, state, or local, regulations.

	CONVENTIONAL FORMULATION	SUPERCRITICAL FLUID FORMULATION
PRICE PER GALLON (coating)	\$18.23	\$26.63
PRICE PER GALLON (reducer)	\$4.28	\$0.00
SOLVENT REDUCTION	100%	NONE
*PRICE PER GALLON (CO ₂)	NONE	\$ 0.58
PRICE PER GALLON (applied)	\$11.26	\$17.21
Theoretical COVERAGE (applied)	152 ft ² /gal	449 ft ² /gal
COST/FT ² (@ 100% Transfer Efficiency)	\$0.074	\$0.061
COST/FT ² (@ 30% Transfer Efficiency)	\$0.247	\$0.183

^{* -} PRICE PER GALLON (CO₂) is based on a 30 weight percent reduction of the coating with CO₂ with the cost of \$0.25/pound of CO₂.

The significance of the comparative data can be better understood with the realization that the supercritical fluid spray process has repeated demonstrated superior transfer efficiencies to the air spray process for which the conventional coating was formulated. It is not unreasonable to expect, in light of the transfer efficiency studies done, efficiencies in the range of at 50% for the supercritical fluid spray process. Given that, the economics are even more dramatic.

	CONVENTIONAL FORMULATION	SUPERCRITICAL FLUID FORMULATION
VOC (applied)	6.24 lb/gal	4.97 lb/gal
Theoretical COVERAGE (applied)	152 ft ² /gal	449 ft ² /gal
TRANSFER EFFICIENCY (probable)	30%	50%
COST/FT ²	\$0.247	\$0.122

The data shows that for this particular coating, a mere twenty percent reduction in VOC realized by utilizing the supercritical fluid spray process translates to a fifty percent reduction in cost per square foot of coverage for the applied coating. Applying the aforementioned principle regarding cost reduction and coating improvement - it is clear that the supercritical fluid spray coating is twice as good as its conventional precursor.

COATING SYSTEMS

The supercritical fluid spray technology has been used to apply a variety of high-quality clear, pigmented, and metallic coatings using thermosetting, thermoplastic, air-dry, and two-pack polymer systems. Polymers that have been successfully demonstrated include acrylics, polyesters, air-dry alkyds, urethanes, melamines, phenolics, vinyls, epoxies, ureas, nitrocellulose, and cellulose acetate butyrate. A wide variety of pigments and filler materials have been used, including many colored organic and inorganic pigments, titanium dioxide, carbon black, aluminum flake, calcium carbonate, silica, and clay. Most polymers and pigments used in conventional solvent-borne coating systems are believed to be applicable to the supercritical fluid spray process. For many applications, little or no adjustment will be needed in the polymer system; only the solvent-blend will need reformulated.

CONCLUSION

Commercial production experience has clearly demonstrated that significant reductions of VOC emissions can be made in coatings using the supercritical fluid spray process. Contrary to conventional wisdom, the results also clearly show that, when using the supercritical fluid spray process, these reductions in pollutant emissions are also characterized by significant improvement in the quality of the coating and dramatic material and operating cost savings to the coating applicator.

The supercritical fluid spray technology has been shown to be an effective pollution prevention technology that is applicable to most types of solvent-borne coating systems. Volatile organic emissions have been reduced up to eighty percent and air toxic solvent emissions have been eliminated in most coatings reformulated for use with the technology. It is expected that solvent emissions will continue to be reduced as new coating systems are developed that have improved carbon dioxide solubility. Eventually, the technology is expected to become the liquid analog to powder coatings but to have better coating performance and significant application advantages.

Commercial use is expected to continue to expand because the process can be an effective replacement for conventional high-solids coating applications that use air, HVLP, air-assisted airless, airless, and rotary spray systems. Besides plastic coating applications, the technology is currently in place in the market areas of wood furniture, automotive topcoats and components, general industrial, adhesives, and release coatings. Continued expansion in the existing market segments, and penetration into the areas of aircraft, metal office furniture, marine, drum, appliance, and specialty applications, is expected in the near future.

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(Expanded Abstract; Paper Not Available) UTILIZING DISPERSION RESINS WITH INORGANIC SOLIDS IN A NEW FORMULARY BLENDING PROCESS TO ACHIEVE SYNERGISTIC RESULTS OF PERFORMANCE

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In attempting to assess the dispersion performance of water-borne acrylic, urethane, and vinyl resins, certain liquid compounds and graded solids regarded commonly as pigments and fillers were employed. Dispersing these materials without adding to the volatile content, various surfactant/detergents were used. Microscopic investigation yielded what we considered unsatisfactory results. As a comparative standard, we then employed textbook formulae in conjunction with these materials. Investigation of dispersion effectiveness was less complete than what had been done prior without the use of added volatiles. Because of experience in other areas of study, it was decided to utilize a blending technique as a developmental endeavor. It is this method which will be discussed. We have come to realize the far reaching effect this can have for the asset protection market; complete blending adds to the life of an applied coating exponentially. There is much to yet be done in this field as the extensive patentability is still underway and as is the perusal of the technical aspects for the explanation of the forces at work.

As conventional blending requires the use of additional compounds, which are undesirable as impactors to the quality of life as air and water contaminators, a blending sequence was laboratory instituted which demonstrated that highly effective mixing could be achieved in much less time than required conventionally. Not only was it found that particle size was reduced without the need for grinding, but compounds could be alloyed that expressed no affinity for one another. Moreover, minimum amounts of active materials suffice for performance when functionally dispersed.

Through a hydraulic extrusion in excess of 12,000 psi, a polyether dispersion, in conjunction with calcium, was driven across an orifice of novel design. This orifice was housed at the front of a tube which acted as a pressure reducing respository. The construction of the tube allowed calibration of a harmonic resonance. We found that resonances are particularly unique to each compound. It was not until explanations for the especially fine compounds produced defied logic that it was deduced that synergism between the shear at the orifice and the staged resonance was acting molecularly to set the ingredients at proper limits to their ionic charges. The visible effects of dispersion and the reduction of particle size achieved a finished material with exceptional layout and physical performance properties. The time

savings to produce the finished article appears to be in the range of 60 to 80 percent. Exotherming, common to paint manufacturing and which limits the total blending completeness of finish, is no longer an issue.

Further calculation relative to orifice/resonance configurations achieved dramatic conclusions. It was at this time that various compounds, which we knew to be immiscible, were applied to the process. Alloys were achieved which performed in extended form as their concentrated counterpart did.

We reviewed the findings of our results and formed conclusions pertinent to physical and social qualifications:

- Conventional blending by shear blades in open tanks can be replaced by closed tanks moving materials by centrifugal pump across a shear orifice, reducing manufacturing air and personnel impact.
- Logistics of manufacturing efficiency can be further improved by the introduction of fluidized ingredients immediately downstream of the orifice.
- A superior finished product with the reudction of undersirable chemicals can be produced in less time with less energy and manpower.
- Alloys of dissimilar materials known to have no affinity can be produced which achieve superior performance of asset protection with economy and ease of application (i.e., hand-rubbed, true perfluorinated wax).
- The where-with-all to realistically bring these findings of fruition for scale production will require concentrated effort and assets.
- Product yielded by this sequence achieves a balance of components which has yet to be explained from a molecular standpoint. After the initial protections are in place to allow a request for funds from standard sources, we plan to develop our discovery further.

SESSION 3

POWDER COATINGS

PAPERS PRESENTED:

"Advantages of Powder Coating"

by

Albert Holder

Naval Surface Warfare Center

Annapolis, Maryland

"Aerospace Applications for Powder Coating at Hughes Aircraft Company"

Larry W. Brown
Hughes Missile Systems Company
Tucson, Arizona

"Fluoropolymer Coatings for Architectural, Automotive & General Industrial Applications"

by

David M. Grafflin

Market Manager - Coatings

Evodex Powder Coatings

Dexter Automotive Materials Division

Birmingham, Alabama

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ADVANTAGES OF POWDER COATING ALBERT HOLDER NAVAL SURFACE WARFARE CENTER ANNAPOLIS, MARYLAND

ABSTRACT

Powder coating, a curiosity only a short while ago, has turned into a 17% per annum growth item in the United States. How did this happen? The equipment manufacturers improved the efficiency and equipment was custom made on request, the powder manufacturers themselves invested in significant research and development, but it would be fair to say that the EPA (Environmental Protection Agency) inadvertently did the most to advance this technology by reducing allowable volatile organic compound (VOC).

The Federal Government, while slow to change, has invested substantial time and money, and is using the products. For example, the Navy coating maintenance facilities on the east and west coasts are increasing their usage. Why this sudden interest? One hundred percent solids, no waste on over spray, dry film thickness from 0.8 mil to 300+ mils, pencil hardness of 6H, are good enough reasons. But most of all, when we recognize that near zero VOC is definately coming. A survey of the options indicates that for those components where fusion of the coating is feasible, powder coating is a good way to go.

INTRODUCTION

Thermoplastic powder coating has been commercially available since the 50's, but not in a refined form. Particle sizes were

never consistent, the equipment was adapted to powder coating or was very expensive. Re-tooling of paint shops was never required in the budget.

Then in the 60's, thermoset powder coatings came into the market with better control of particle size. The finished product looked like liquid paint and in most instances, their properties were superior.

Still progress was extremely slow in introducing the technology into paint shops, because of the initial high expense. There was no necessity to change, as liquid paints were being made to their specifications or custom made for the old equipment.

Then came environmental regulations, as administered through the EPA. The agency's primary function is to control, monitor, advise and even fine if necessary, any organization or person violating the federal laws on exceeding the limits for pollution of the air and water. In our coating industry VOC, toxic chemicals, and pigments are of concern. As important is the disposal of waste created during manufacture and application. Disposal sites are diminishing in numbers, therefore supply and demand is inflating the cost of disposal. Waste created is the responsibility of its creator to the very end. With this in mind management was making an effort to adjust or shutdown. and coatings with lower VOC's like high solids, waterbased coatings, and powders were all potential replacements. High solids and waterbased coatings still produced overspray and higher loss than powder coating, which has a 96-99% transfer efficiency. Waste and pollutants are minute in comparison to

conventional paints.

Equipment manufacturers have done their homework and introduced new spray guns, spray booths, extruders, mixers, etc., by improving efficiency and custom-building of units. Many paint shops are required at this point in time to replace old equipment, and those who went with powder are very encouraged.

ECONOMIC ASPECTS

Powder coating is a proven compliance technology, with negligible overspray loss, no waste, because it can be recycled.

Is it difficult to formulate? No! Liquid coatings can be much more time consuming, with a great variety of ingredients.

The composition of powder coating versus conventional paints are compared below:

POWDER COATING	LIQUID COATING
PIGMENT(S)	PIGMENT(S)
POLYMER(S)	POLYMER(S)
CATALYST(S)	CATALYST(S)
ADDITIVE(S)	ADDITIVES
• •	SOLVENTS

For powder coatings the polymer and catalyst can be purchased as one resin. Liquid coatings for baking generally contain more than one polymer, two or more solvents and usually more than one additive.

MANUFACTURE

POWDER COATING	LIQUID COATING
COLLECT INGREDIENTS	COLLECT INGREDIENTS
PREMIX ·	DISPERSE
EXTRUDER	LET DOWN
CHIPPING	ADJUST VISCOSITY
GRINDING	PACKAGE
PACKAGE	

Without a doubt, raw material collection for manufacture of liquid paints or coatings is more labor intensive due to the greater number of ingredients and the fact that additions can only be made at certain intervals during manufacture.

APPLICATION

There are two common methods:
FLUIDIZE BED
ELECTROSTATIC SPRAY

TYPES OF RESINS

THERMOPLASTIC THERMOSET

The thermoset resins or polymers in the future will be used in place of non-compliance VOC coatings such as epoxy polyamides.

REACTION OF POLYMER TO HEAT

<u>THERMOPLASTIC</u>	THERMOSET
MELT	MELT
FLOW	FLOW
GEL	GEL
	CURE (NO REMELT)

COMMON THERMOPLASTIC AND THERMOSET POLYMERS

WEIGHT)

POLYPROPYLENE EPOXY
POLYETHYLENE POLYURETHANE
NYLON ACRYLIC
PVC POLYESTER (LOW MOLECULAR
POLYESTER (HIGH MOLECULAR
WEIGHT)

Liquid coatings have alkyd resins as the workhorse, powder coatings have epoxy resins. Epoxies can give thin or thick films and therefore, can be used for decorative or functional purposes. They are chemical resistant and FDA approved.

Polyester polymer modified with epoxy resin, polyurethane, or triglycidyl isocyanurate gives properties not achievable by the individual polymers.

Acrylic resins are usually used in combination with blocked urethanes and have excellent gloss, thin film appearance, and hardness with only fair impact resistance.

PROPERTIES OF THERMOSET POWDER COATINGS

POLYMER	HARDNESS PENCIL	IMPACT (INCH-LB)	SALT-FOG (HOURS)	EXTERIOR DURABILITY	CURE (DEGREES	F/MINS)
*EPOXY	нв-5н	60-160	1000	POOR	450/3 250/30	
HYBRID	нв-2н	60-160	1000	FAIR POOR	450/3 325/25	
POLYESTER	нв-зн	60-160	1000	GOOD VERY GOOD	400/7 310/20	
ACRYLIC	HB-3H	60-160	1000	GOOD GOOD	400/10 360/25	

^{*}Re-bar epoxies are cured 450/25 seconds.

THE ADVANTAGES OF POWDER COATING ARE CONVINCING.

Powder coating shows both technical and economic advantages in comparison to other processes, while lowering coating costs, quite considerably, reducing production risks and are

- --economical--thanks to powder recovery
- --harmless to the environment--no solvents
- --more durable against mechanical influences
- --cleaner to work with--no solvents
- --easily automated thanks to wrap around
- --high build films--achieved in one operation

WHAT ARE THE PROCESS REQUIREMENTS FOR POWDER COATING?

- 1. Suspension of blank parts
- Pre-treatment (i.e. de-greasing, phosphating, chromating)
- 3. Drying
- 4. Powder coating
- 5. Baking 275-450 F
- 6. Removal of cured parts

MARKET SECTORS

TRANSPORT -AUTOMOTIVE

-TRUCK & BUS

DOMESTIC

-WHITE GOODS

APPLIANCE

-HEATING

-FIRES

-LIGHTNING

BUILDING

-ALUMINUM EXTRUSIONS

-CONSTRUCTION PARTS

-STRUCTURAL STEEL/ALUMINUM

ELECTRICAL

-LIGHT/ELECTRONICS

-SWITCHGEAR

GENERAL INDUSTRIAL -TRADE COATERS
-OFFICE FURNITURE

-BUSINESS MACHINES

-SHELVING AND RACKING

-GARDEN FURNITURE

PUBLIC

-STREET LIGHTNING

SERVICE

-FURNITURE

HEAVY

-REBAR

DUTY

-GENERAL HEAVY DUTY

-PIPELINES

NAVY AND POWDER COATINGS

The Navy has Naval shipyards and Shore Intermediate

Maintenance Activities at various locations on the east and west

coasts that apply powder coatings. In these activities, shops

are set aside for corrosion control and it is here that powder

coatings are being used or seriously considered for production

purposes.

Parts and components are received daily from ships and are immediately:

⁻⁻Logged

⁻⁻ Tagged for identification

⁻⁻ Degreased with trisodium phosphate

⁻⁻Blasted with abrasive, usually aluminum oxide, to near white metal

⁻⁻Preheated

⁻⁻Powder coated 10(+ or - 2) mils thick

⁻⁻Post heated

Surface profiles for steel and aluminum are two to three mils and one to two mils respectively.

Epoxy powder coatings have proved very efficient for Navy use. The Naval Sea Systems Command (NAVSEA) has designated powder coatings for shipboard corrosion prevention and control and is currently conducting testing and evaluation on the feasibility of using powder coating as sealer and top coating for thermal spray aluminum. With the longer service life of the coatings, Naval personnel will have more time for the ship essentials like training and vital operations.

Powder coatings are less permeable, which is very important in our case, have short baking times and produce almost no pollutants or hazards, since no solvents are involved.

Five years of use in corrosion control application has proved substantially positive. Some of the areas now employing powder coatings are:

- --Vent Screens
- --Telephone Boxes
- --Electrical Boxes
- --Light Fixtures
- --Lockers
- --Bunk Beds
- --Search Light Fixtures
- -- New Construction
- --Battle Helmets
- --Or Any Portable Housing
- --Valve Bodies

The Navy sees a substantial increase in the use of these coatings in the never ending battle to prevent or retard corrosion.

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

AEROSPACE APPLICATIONS for POWDER COATING at HUGHES AIRCRAFT COMPANY

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INTRODUCTION

Regulations restricting Volatile Organic Compound (VOC) emission and hazardous waste generation and disposal are beginning to seriously impact the painting of aerospace hardware. Continued use of many of the traditional aerospace paint systems such as the Mil-P-23377 Epoxy Primer / Mil-C-83286 Urethane Topcoat has been prohibited in many areas of the country since they exceed 420 gm/liter VOC content. Some users of the new compliant paint systems have experienced significant paint related cost increases due to additional rework, more stringent record keeping, and increasing hazardous waste disposal costs.

Hughes Missile Systems Company (formally the Missile Systems Group of Hughes Aircraft Company) began working with powder painting in 1983 while searching for improved painting processes. Since the powder painting process produces essentially no VOC's and reduces hazardous waste generation, it offers significant environmental advantages over competing paint systems including compliant systems that reduce the level of emissions. The Navy approved powder paint for use on the interior of the Phoenix missile fuselage in 1986 and these have been successfully powder coated since that date. Additional development work has led to several more powder paint applications and successful implementations on both the Phoenix and Maverick missile programs.

Organic coatings (paints) serve a wide variety of functions in the missile industry. Exterior surfaces as well as some interior areas of missiles normally receive some type of organic finish. The customer specifies the required finish system based on the requirements of each service branch or application. The primary function of an organic finish system is for protection from environmental influences. Other associated functions include visibility characteristics and missile identification for tactical or training purposes. Thus an organic finish system is an important aspect of missile manufacturing.

Conventional liquid paints use solvents to transport the pigments and resins over the surface to be painted. After the volatiles evaporate, only the pigments and resins that form the final painted surface remain. Since these volatiles comprise a significant portion (30% to 80%) of the applied paint film, only a fraction of the applied material forms the dry paint film.

Powder paint, by comparison, consists of blended resins and pigments ground into a very fine powder. During application this powder is fluidized and usually electro-statically sprayed on the part being painted. The cure process uses an oven at temperatures ranging from 250°F to 400 °F to fuse the paint particles to each other and bond them to the substrate. Since there are essentially no volatile components (significantly less than 1%), all of the applied paint material becomes part of the dry paint film.

Since the early 1980's powder painting has experienced tremendous growth averaging almost 20% growth per year in terms of quantities of powder sold! Powder painting is used in many commercial applications including appliances, automobiles, office furniture, architectural applications and sporting equipment. The paint performance requirements for many of these applications are similar in many respects to the performance required of aerospace coating systems.

POWDER PAINT MATERIALS

There are two major classifications of powder paint, thermosetting and thermoplastic. Thermosetting powder paints cross-link chemically to produce higher molecular weight materials during the thermal cure process². As the material cures, it chemically cross-links and will not reflow upon re-heating. A thermoplastic powder however will melt and flow upon application of heat, but is chemically unchanged; thus when reheated it will re-flow.

Thermoplastic Powder Coatings

Thermoplastic coating materials include polyethylene, polypropylene, nylon, polypropylene, and thermoplastic polyester. Thermoplastic powders are generally used for special applications requiring thick films and they do not normally compete for the same applications as liquid paints. The high molecular weight resins used in thermoplastic powder paints are difficult to grind to the small particle size necessary for the spray application and fusing of thin (less than 5 mils) films. These coatings are selected for their chemical resistance, electrical insulation, weather ability, abrasion resistance, or low coefficient of friction.

Thermosetting Powder Coatings

Since thermosetting powder paints chemically cross-link during the curing process to form higher molecular weight products, the cured coating has a different structure and properties than the basic resin. Thermosetting powders can be ground into fine particle (25 - 40 microns average) and can form thin paint coatings in the 1 to 3 mil range. These powder paints compete for the same market with available liquid paints since they produce surface coatings with properties equivalent and sometimes superior to the coatings produced by the liquid compliant technologies. A technological expansion has occurred in the area of thermosetting powder paints in the last few years. The major types of thermosetting powder paints are: epoxy, epoxy polyester hybrid, urethane polyester, and acrylics

Epoxy Resin Powders

Epoxy resins are utilized by most thermosetting powder paints in use today. This class of powders offers excellent chemical resistance, toughness, flexibility, adhesion, and corrosion characteristics. Advances in epoxy formulations have enabled epoxy based powders to be tailored to a wide range of desired film characteristics. Additionally, epoxy powders can be formulated to cure over a wide range of bake temperatures some with cure temperatures as low as 250° F. Epoxy powders cost less than other available powder formulations.

Unfortunately, epoxy powder paints share liquid epoxy paint's limited ultra-violet (UV) resistance and thus chalking of the paint surface is the result of extended exterior exposure. An epoxy powder paint will chalk within a few months of exterior exposure. This chalking does not significantly affect the paints excellent physical, chemical resistance, or corrosion protection properties. Chalking is a surface phenomena and inhibits further degradation. Cleaning will restore much of the original paint finish but will allow additional chalking to occur. Chalking is most noticeable on high gloss dark colored paints, while it is least noticeable on light colored low gloss paints. In addition to having equivalent or superior properties, epoxy powders generally cost less and can be formulated to cure at lower temperatures than other powder materials.

Epoxy Polyester Hybrid Powders

These hybrid coatings were developed in Europe as an attempt to improve the weather ability of epoxy powders. They are closely related to epoxy powders and have similar properties. Hybrid powders have improved over-bake and weather ability characteristics. They still chalk but the rate of chalking is slower and results in less discoloration than standard epoxy powders. Hybrid powders provide corrosion protection similar to epoxy powders, although they have softer films and generally demonstrate a reduced resistance to solvents and alkali. These powders have excellent electrostatic spray characteristics and demonstrate improved penetration into corners and recesses relative to other powder coatings.

Urethane Polyester Powders

Urethane polyester powders are comparable chemically to the exterior quality urethane paints which have been used on aircraft, buses, and other vehicles for a number of years. These films combine toughness with excellent weathering characteristics. These coatings must be applied in thin films (less than 2 mils) or the mechanical properties, such as impact resistance and flexibility, tend to be degraded. These coatings are good candidates where exterior durability is required.

Acrylic Powders

The final group of thermosetting powder coatings is the acrylics, which exhibit excellent exterior durability. The acrylics generally exhibit excellent hardness and good impact resistance along with excellent alkali resistance. However, acrylics generally exhibit inferior adhesion characteristics as compared to other powders. Acrylic powders are usually more expensive than other powder coating formulations.

APPLICATION CONSIDERATIONS

Unlike liquid painting technologies, powder painting may not be applicable to every part or assembly. Since powder paint is usually applied by electrostatic spraying, the surface being coated needs to be conductive or have a conductive layer a few mils under the surface. This conductive layer is grounded during the application process and the charged paint particles are electro-statically attracted. A conductive wash may be applied to non-conductive parts, such as composite materials, to provide a temporary conductive layer sufficient to provide electrostatic attraction of the paint particles. After the paint particles have been electro-statically applied, the ground may be removed and the powder particles will maintain adhesion during normal handling.

Powder painted parts or assemblies must be capable of being baked at the powder paint's cure temperature. Cure temperatures range from about 250°F for a low temperature epoxy powder paint to over 400°F for some other powder formulations. Although powder cure times are short, 5 minutes to approximately 45 minutes, they are at peak temperature; therefore a massive part must also be allowed the time necessary to reach temperature in addition to the cure time. Required cure duration is generally inversely proportional to cure temperature. Since powder paints usually have excellent abrasion resistance, powder painted parts usually require little or no touch-up after typical assembly processes. These abrasion characteristics allow components to be powder painted prior to assembly, thus avoiding thermal damage to sensitive components or assemblies.

The part geometry should also be evaluated to identify areas which may be difficult to paint due to Faraday cage effect³. These areas can usually be painted successfully, but some experimenting with application process parameters (atomizing pressure, powder flow rate, voltage, etc.) and spray application geometry may be necessary. Some substrate materials or surface treatments may also require experimentation to insure acceptable paint film characteristics.

Due to the chemical resistance of some powder coatings, they usually cannot be effectively removed using solvents or paint removers. Removal usually requires some form of media blast to eliminate the paint economically. Media blast must be carefully evaluated before using it in applications where non-destructive testing techniques are used, since it may obscure cracks, corrosion or signs of metal fatigue.

ECONOMIC CONSIDERATIONS

Powder painting offers several potential economic advantages when compared to liquid painting technologies⁴. Savings can be realized in the areas of labor, energy, material, hazardous waste disposal, and safety. The savings in several of these areas are sometimes difficult to quantify, however, when analyzed and added together, the powder system usually offers a significant cost advantage over liquid coating systems. Table 1 summarizes the approximate costs per square foot for a traditional manual liquid painting operation and a manual powder painting facility. These costs are very sensitive to part complexity, painted area and lot size and the data in Table 1 assumes a complex geometry totaling a few square feet of painted area flowing through the painting operation in lot sizes of approximately 10.

3 COAT LIQUID SYSTEMS	\$/SQUARE FOOT	POWDER PAINT	\$/SQUARE FOOT
LABOR	2.00	LABOR	.50
		MATERIAL	.15
MATERIAL	.30	ENERGY .	.05
ENERGY	.05	WASTE	.05
WASTE DISPOSAL	.15	DISPOSAL	
TOTAL COST	2.50	TOTAL COST	.75
POWE	ER PAINT	COST SAVIN	GS =
		1.75 / SQUAR	

Table 1: Cost Comparison - 3 Coat Liquid Paint System vs Powder Paint

Labor Savings

Labor savings associated with powder painting result from several factors. First, powder paints are delivered ready to use and require no mixing with solvents or catalysts. This eliminates an entire operation usually associated with liquid coatings. Additionally, monitoring and maintaining many process parameters associated with liquid painting (viscosity, pH, solvent content, percent solids, etc.) is unnecessary. Powder painting is usually a one coat application. and significant labor savings result from eliminating the application of primer and multiple top Powder painting requires less operator skill and training than normally coat applications. required for liquid painting. Since the powder particles can be removed from the part with compressed air prior to baking, it is very easy to rework parts prior to cure. After the parts are cured, any required touch-up can be performed using a compatible liquid paint. Clean-up of the paint gun and booth is much easier with powder paints and require only a broom and compressed air, and vacuum cleaner instead of the solvents and wipe cloths required to clean-up after solvent based liquid painting. In some applications powder painting may eliminate up to 75% of the labor required for liquid painting.

Energy

Significant energy savings can be realized from the implementation of powder painting. Since the quantity of volatiles in powder paints are minimal and no room temperature volatiles are present, the makeup air requirements can be dramatically reduced. No makeup air is required for the powder paint booth and only small amounts are required to vent the ovens used for curing. This translates into a significant savings in air conditioning or heating. While the oven temperatures required for powder painting are significantly higher than normally used to cure liquid coatings, the cure time is significantly shorter. Thus there is usually an energy savings resulting from implementing powder coating.

Material Costs

The increased material utilization advantages possible using powder coatings usually result in material cost savings when compared to liquid coating systems. An electro-statically applied powder paint will achieve approximately 70 percent first pass material utilization. The oversprayed powder particles can be collected, screened and then mixed with virgin powder for reuse. Since less than 1 percent of the applied material is volatile, powders easily achieve material utilization rates of about 95 percent. Liquid systems usually achieve overall material utilization rates of between 20 to 60 percent since the over-spray cannot be recycled and the sprayed material contains large quantities of volatiles.

There are fewer materials to store since powder coatings usually replace both the primer and topcoat. Most powder paints can be stored in room temperature environments (65° to 85° F; < 50% Relative Humidity) however low temperature cure powders (< 300 ° F) may require refrigerated conditions. Shelf life for properly stored material may vary from 6 to 12 months for low temperature powders to several years for other formulations.

Since drips and runs are almost nonexistent with powder painting, the reject rate typically declines, resulting in higher yields. The cured powder paint film usually has better abrasion characteristics than liquid paints. This enables powder painted parts to withstand handling and assembly with less paint damage, thus resulting in reduced rework. Additionally, cleanup of spray guns and paint booths used for powder painting requires no solvents and is therefore safer, cheaper and easier.

Environmental Costs

Significant quantities of flammable hazardous materials, including cleaning solvents, mixed paint, catalysts, etc., are associated with liquid painting systems. These require special handling, storage, and disposal. The need for these solvents and other flammable hazardous materials is eliminated when using powder coatings. The quantity and type of hazardous waste generated from a powder coating operation is dependent on the type of powder, resin formulation and pigmentation (metallic) constituents. Powder paint formulation sources indicate that modern powder paints should pass the Toxicity Characteristic Leaching Procedure (TCLP) testing and alternatives to disposal as hazardous waste of excess or used powder may be available depending on local regulations. Therefore, to ensure proper disposal, the waste classification or listing should be determined on a case by case basis. Powders have several environmental advantages when compared to solvent based liquid coating systems. These advantages, including greatly reduced solvent use, lower fire hazard, and greater operator safety, provide a cost advantage when comparing powder painting to other painting systems. The cost and liability associated with waste generated from a powder coating process may be considerably less than a solvent base painting system.

In many areas, the use of certain liquid coatings is either prohibited or requires the installation and operation of expensive adsorption devices to remove VOC's from paint booth and oven exhausts. The lack of volatiles in powder paints eliminates this problem and may significantly reduce the fire risk. Powder paints also result in a much cleaner environment for paint shop employees, and may lower labor costs by reducing the overhead associated with safety equipment and allowing a lower job class employee to perform the task.

HUGHES MISSILE SYSTEMS COMPANY (HMSC)

The standard liquid paint system used at the HMSC Tucson plant site is the Mil-P-23377 epoxy primer and the Mil-C-83286 Urethane topcoat. A Mil-C-8514 wash primer is also used on some alloys including inconnel. Prior to 1986 all production hardware was painted using these or similar high-solvent liquid paints. HMSC began evaluating powder paint in 1983 and implemented several epoxy powder painting applications on both the Phoenix and Maverick missile systems between 1986 and January 1991. These powder paint applications accounted for approximately 60% of the facilities production painting volume after January 1991.

The typical conventional wet paint process flow chart is presented in Figure 1 with all VOC emission points and hazardous material generation points are identified. On substrates where a wash primer is required several additional operations are required which add additional VOC emission points and hazardous waste generation points to the flow chart. Thus our conventional painting process consists of at least thirteen operations, twelve of which produce VOC emissions and eight of which produce hazardous waste.

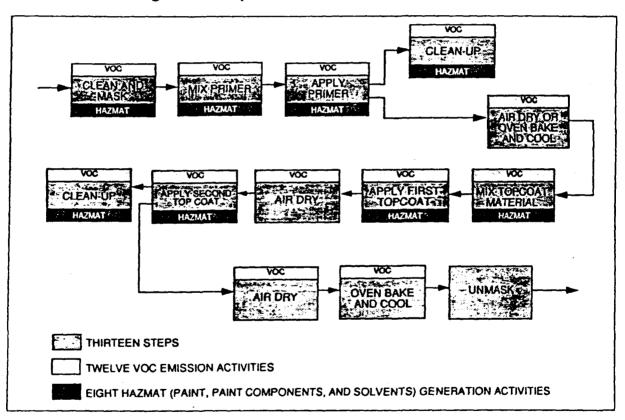


Figure 1: Typical Liquid Paint System Process Flow

Figure 2 shows the epoxy powder painting process which has been used to replace conventional wet painting on several applications at the HMSC Tucson facility. This process consists of only six operations with only one VOC emission point, one hazardous material generation operation and two possible hazardous material (HAZMAT) generation operations.

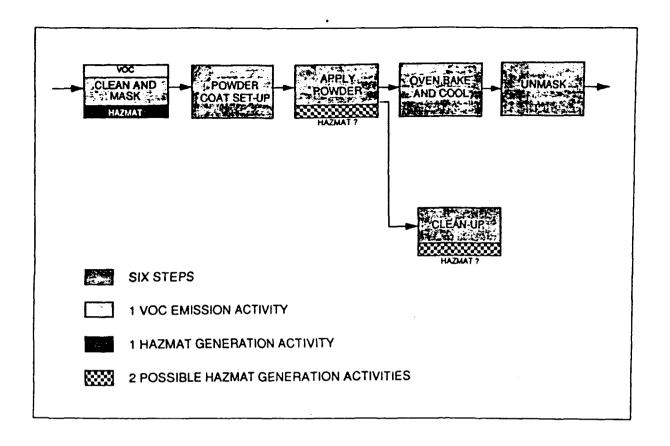


Figure 2: Powder Paint Process Flow

The Toxicity Characteristic Leaching Procedure (TCLP) test data for the powder we use indicates that it can be disposed of as ordinary waste instead of hazardous waste however this needs to be evaluated for each powder paint and regulatory environment. Thus the only VOC and HAZMAT generation point is the cleaning operation prior to painting. By implementing a high pressure aqueous cleaning system this VOC and HAZMAT generation point was eliminated for the powder painting of the Maverick airframe resulting in a paint process with no VOC emissions or hazardous material generation points.

Comprehensive testing has been required to qualify powder paint for all current applications since no Military Specifications cover the application or material performance of powder paint on airborne systems. A portion of the many tests procedures included salt fog, humidity, dry and wet tape adhesion, abrasion resistance, impact, and resistance to various solvents. The selected epoxy powder paint system was typically equivalent or superior to the Mil-P-23377 / Mil-C-83286 paint system which was used as the benchmark. Since no appropriate powder paint Mil-Specs exist, internal specification control drawings are developed and engineering changes specifying powder painting are processed and evaluated on a case by case basis. Although this is a lengthy process, environmental and cost benefits following implementation make the effort worthwhile.

POWDER COATING INDUSTRY

Powder painting systems suitable for most applications are currently available from several suppliers. Most low and medium volume applications can be handled using booths with manual electrostatic powder application guns and no powder re-claim capability⁵. For most applications these systems would use existing batch ovens for curing and could be integrated into existing paint shops. Systems for high volume applications is considerably more expensive since they usually incorporate capability for quick color change, powder re-claim, and monorail conveyor systems feeding the pre-treatment equipment, powder paint booth, and cure oven.

There are over ten major powder paint manufacturers supplying the US market. While most of these have worked with the aerospace industry they primarily supply powders for the automotive, appliance, and industrial markets. All of these manufacturers have powder development laboratories and can formulate small quantities of custom powders for testing. Minimum lot size for custom formulations may range from about 250 to 1500 pounds. Purchasing small quantities of custom powders for low rate applications can be challenging although the situation seems to be improving and one powder manufacturer is specifically targeting aerospace applications. Another powder manufacturer has recently added the capability to supply from stock the full range of Fed. Std. 595a colors in a polyester powder formulation.

Powder Paint Specifications

The only Military Specification for powder painting is Mil-C-24712 "Coatings, Powdered Epoxy" issued by the Naval Sea Systems Command in February 1989. This specification was intended for interior steel and aluminum equipment, furniture, electrical box surfaces and exterior steel and aluminum surfaces exposed to marine environments. The first revision of this specification is scheduled to be issued in the near future and will add polyester powder paints for improved exterior UV resistance. Paints meeting Mil-C-24712 are available from several sources.

Other specifications such as WS 22351 for the Mark 48 torpedo cover powder painting for specific weapon systems. This particular specification was issued by the Naval Underwater Systems Center and covers the powder materials, application processes and test requirements for the ADCAP torpedo.

CONCLUSIONS

Experience at the HMSC Tucson plant site has demonstrated that powder painting consistently reduces the cost associated with painting while essentially eliminating paint related VOC emissions and HAZMAT generation. Although powder painting is not currently suitable for all aerospace applications it is both cost effective and appropriate for many applications. Increasingly stringent environmental regulations tend to favor the long term development and implementation of powder painting since it eliminates both VOC emissions and hazardous waste generation.

The cost savings and quality improvements associated with powder painting has enabled HMSC to be proactive in developing and implementing this environmentally friendly process even in today's competitive environment. Efforts to implement new powder paint applications at HMSC are expected to continue especially since previous powder painting applications have demonstrated cost reductions, quality improvements in addition to eliminating paint related VOC emissions and hazardous waste generation.

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FLUOROPOLYMER COATINGS FOR ARCHITECTURAL, AUTOMOTIVE & GENERAL INDUSTRIAL APPLICATIONS

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The primary focus of this paper is an exciting, environmentally-compliant full-strength fluoropolymer powder coatings technology which combines all of the traditional performance of the low solids solvent-borne PVDF (polyvinylidene difluoride) coatings used primarily in exterior architectural applications and specialty automotive critical fluids tubing requirements in a 100% solids powder coating system. The development of a commercially viable PVDF powder coating for these applications is the direct result of successfully addressing the somewhat unique issues relating to the efficient processing of the raw materials, rather than a modification of the basic chemistry which has been utilized in a liquid, solvent-borne format since the mid-1960's. The high level of performance which this chemistry has demonstrated in terms of the recognized aggressive architectural specifications and its resistance to ultraviolet light degradation, chemical and mechanical attack and automotive fluid resistance requirements, was initially evaluated with great care to determine the percentage of the weight solids of the formulation which needed to be composed of the PVDF component. In an evaluation array which spanned PVDF composition at everything from ten percent (by weight solids) to ninety percent of the formulation, with a variety of copolymer chemistries as the associated vehicle, it was convincingly demonstrated that the PVDF material (effectively dispersed in a solvent vehicle) at a fifty percent level, began to have a positive impact on the performance of the applied film, and that at a seventy percent level, the optimum balance of performance and ease of application was accomplished, and this quickly became the standard of the industry.

At the time that this technology was commercially introduced in its liquid form (through a series of coatings companies who were licensed to utilize the PVDF resin in this marketplace), the fact that this chemistry was self-limited

to a maximum of 35% volume solids, by virtue of the difficulties in dispersing the resin, was a non-issue, as the entire discussion of VOCs and their environmental impact had not surfaced. During the decade of the 1970's and into the early 1980's, the effectiveness of this solvent-borne liquid chemistry continued and flourished, and there were very few efforts directed at moving toward a compliant vehicle. The work which was done was directed initially at a water-borne dispersion of the resin, which proved extremely difficult and ineffective in sprayable formulations, resulting in films which demonstrated inconsistent performance, and which were more difficult to apply due to a tendency of the resin to agglomerate within the coating itself. At the same time, in those applications which were being performed on conventional coil coating lines (the high volume users of this chemistry), the installation of incinerators during the early energy crisis to capture the relatively high solvent levels in these formulations in order to recover the fuel potential in these low volume solids formulations further reduced the interest in a move to compliant chemistries. The remaining segment of the market which was going to have to address this problem was in the spray application end, typically handled by entrepreneurial independent applicators who were, at least at that time, not getting extensive attention from the regulatory agencies.

Against this backdrop of a protected channel of distribution and the limited scope of enforcement activity, there was no driving compulsion for the primary resin suppliers to develop a compliant material. In the automotive tubing market, virtually all of the initial applications for this technology were developed and utilized in Japan with no associated environmental pressure to bring these materials into compliance. The applications were primarily via dip application and were able to coat relatively large quantities of tubing with fairly small quantities of coating which further reduced the visibility of the process as a source of potential environmental liabilities.

In the American architectural metals marketplace, essentially none of the applicators were involved in or particularly aware of powder coatings as a technology, nor were they equipped to apply the material. In Europe, however, the situation was functionally quite different. The architectural marketplace was successfully being supplied with polyester powder coatings, both due to the lower levels of UV exposure present in their environment, and the significantly different infra-structure which had never fostered the growth of a viable PVDF liquid coatings market. The applicators and the coatings manufacturers supplying this market were very comfortable with powder coatings as a technology, and with the somewhat different cosmetic appearance which powder coatings provide (the slight "orange peel" evident in the cured film). For them, the question was whether or not they needed a PVDF powder coating product, as they had never seen their market significantly impacted by the liquid material, nor were their customers demanding a significant upgrade in product quality. The marketplace had grown accustomed to the solid but reduced performance of polyester films when compared to full-strength PVDF films, and they were already environmentally compliant by virtue of functioning in a powder system. They certainly had no desire to make a move to PVDF in any liquid format, either solvent or water borne, as this would be a complete transition in their coatings lines, and their potential interest in a PVDF powder coating was driven by the desire to be able to compete in an increasing global market with a product which met the requirements of the two most environmentally aggressive and growing markets, North America and the Pacific Rim.

It is worth noting that the bulk of the European higher quality requirements were initially being met with TGIC polyester powder coatings. The TGIC crosslinker (triglyceridyl isocyanurate) has become the subject of much discussion in the past two years concerning its potential as a mutagen, based on both inhalation and ingestion studies in Europe and the United States. After extensive testing and great public debate which was leading the coating suppliers

to evaluate and to commercialize non-TGIC polyester systems, a re-evaluation of the test data has led to a minimization of the concerns, and in fact, in many markets, the pressure has essentially disappeared concerning the elimination of this material. The alternative crosslinkers which have been evaluated are competitive in performance at essentially equivalent cost, but given the lack of extended exposure and test data with them in formulated coatings, there has been reluctance to move forward with a wholesale change given the reduced pressure from a hazardous materials perspective.

Sigma Coatings, B.V., in the Netherlands, who had significant commercial activity in PVDF liquid coil coatings and polyester powder coatings for the architectural marketplace, became seriously interested in the potential for a PVDF powder coating in the early 1980's, and undertook a research project in their facility in Zeist which quickly arrived at the same functional hurdle which the preliminary efforts in the USA had identified in similar attempts earlier—the complexity of this issue was not in its chemistry (the formulas of the two versions of this technology are identical), but in the efficient processing of this material, given the thermoplastic nature of the resin, in order to make its application economical, and competitive to the liquid formulations well-established in the marketplace.

Traditional thermosetting powder coatings are manufactured in a dry blending process in which the ingredients are measured, and blended together prior to being introduced into a modestly heated extruder from which they emerge in a viscous condition, are rolled out into a ribbon which is cooled and cracked into chips or flakes, and subsequently introduced into a conventional grinder which reduces the material to the fine particle size distribution which is typical of powder coatings. If this same procedure is utilized with PVDF chemistries, their thermoplastic nature survives in traditional processing up until the material emerges from the extruder. At that point, the material is thoroughly incompatible with room temperature grinding as it rapidly melts into a taffy-like mass which resists further processing.

The technical approach taken by Sigma Coatings was directed at simplifying the processing of this material in light of its thermoplasticity, and toward developing a mechanical sequence which resulted in a high percentage through-put of a viable material. The first significant change came at the exit of the extruder, where rather than extruding the blended powder coating out through chilled rolls in a ribbon-like format, the extrudate is forced through a water-chilled die so that it resembles uncooked spaghetti strands which can then be chopped into small semi-rigid pellets for further processing.

After a series of empirical evaluations, it was rapidly determined that conventional water cooling was not sufficient for effective processing of this material into a usable product, and work was begun on identifying the most appropriate cryogenic temperatures at which a workable material could be manufactured. The results of this work (now well-documented in two US patents issued in 1986 and 1989) demonstrated that pre-cooling the pellets produced in the extruder by immersion in liquid nitrogen at approximately -50°C., and introducing them into a grinder charged with liquid nitrogen at a volume which maintains the pellets at approximately -125°C. throughout the grinding process, yielding in excess of ninety-seven percent usable product. The powder which is produced is predominantly in the 40-55 micron particle size distribution range. and once applied, demonstrates superior film flow and leveling, resulting in a cosmetically attractive film which provides all of the performance of the traditional solvent-borne materials, and reduces their approximately 6.5 pounds per gallon of VOC's to almost nothing. In addition, by the nature of the chemistry, the finished PVDF powder coating is extremely compatible with electrostatic application (either corona or tribo), and applies effectively at extremely low voltage and air settings on any available powder coating equipment.

No conversion of technology such as this happens easily, or with direct translation of all of the benefits of the former system into the new one. Powder coatings, by virtue of their composition and format, will never be able to replicate the blending systems readily available in their liquid counterparts which make possible the combination of base colors into custom colors in very small batches. In addition, the liquid clear coats which are produced in liquid fluoropolymer chemistry as an adjunct coating to the color coats are not possible in powder, as the exposure to liquid nitrogen hazes the material irreversibly and imparts a cloudiness to the applied film which is cosmetically and functionally unacceptable. In addition, it is more difficult to produce brilliant metallic colors in this technology through the typical powder coating bonding process as it tends to fuse the thermoplastic material unacceptably, while dry-blended PVDF metallics are certainly viable. Beyond these few limitations, it is important to repeat that the color space of PVDF coatings, either powder or liquid, is EXACTLY the same by virtue of the fact that the pigmentation utilized to deliver the performance mandated by the architectural specifications which typically call for this material (American Architectural Manufacturers Association 605.2, etc.) is identical. These ceramic pigments, which demonstrate tremendous stability in extended UV exposure, and deliver the high levels of color and gloss retention demonstrated by PVDF films, are identical in the liquid and powder formulations, assuring that the colors are the same in the final films. The resin which is the backbone of these PVDF coatings, traditionally known by the tradename of its producer (Kynar 500® as produced originally by the Pennwalt Corporation, more recently acquired by Elf Atochem North America, Inc.), is different in its particle size depending on whether the vehicle is to be powder or liquid. Kynar 500°, when provided for powder coating use, is provided in a finer particle size under the tradename Kynar 500PC. The chemical composition of the resin is unchanged, as is the performance of the applied film, as measured in all of the traditional measures of architectural performance.

The longest term measure of performance, and the single criterion which most specifically separates full-strength PVDF films from their lesser counterparts, is the stability of these coatings in extended exterior exposure. The traditional measurement in the architectural market is color and gloss retention after five years of exposure in South Florida at a 45° angle. first panels of liquid PVDF films went on exposure in early 1964, and there are literally thousands and thousands of such panels still on exposure, amply demonstrating the performance properties of this material. The first panels of powder PVDF films went on similar exposure in April of 1986, and as of this meeting are now over seven years old, and are demonstrating all of the performance characteristics of their liquid counterparts in terms of exposure. In accelerated testing, the powder films meet and exceed all of the physical testing standards, with the superior performance most associated with the fact that the powder coatings tend to develop a thicker film than their liquid counterparts (1.6-1.8 mils total film versus 1.0-1.2 mils total film), with the advantages seen most often in falling sand resistance, transit abrasion and handling damage improvement, preferable pencil hardness, and more uniform deposition on formed radii and shapes.

The thermoplastic systems described in this paper are applied as the last step of a total finishing process for architectural substrates. From the pretreatment perspective, the requirements for proper cleaning and either chromate or chrome-phosphate conversion coatings, remain the same in powder as they are in liquid. There is a requirement for a traditional primer chemistry, available in either a liquid flash version or a powder cured vehicle, under the PVDF powder coatings. The specific gravity of the PVDF powder coatings is relatively high, typically 1.7, which sees applications efficiencies on line with proper voltage and air controls, at the level of 60 square feet of coverage per pound of powder applied or more, with extremely high first pass transfer efficiency given the electrostatic affinity of this material to which we have already referred.

With the demonstration of a viable thermoplastic PVDF powder coating for monumental architectural applications, the industry now has a full range of environmentally compliant technologies with which to address the emerging enforcement of the 1990 Clean Air Act and its amendments. From the conventional TGIC polyesters on which this market segment was founded in Europe, to the emergence of the functionally equivalent non-TGIC polyesters which resolve the potential for any mutagenic concerns during application, to the presence of the PVDF films, there is now a range of product qualities available which meet and exceed the requirements for commercial/light industrial/low-rise architectural specifications (AAMA 603.8 typically), right through monumental architectural specifications as discussed (AAMA 605.2 typically). It is worth re-stating that the performance of these materials and the differences between them is the same in powder as it is in liquid, as the chemistries neither gain nor lose properties by virtue of their physical state. The greatest differences in gloss and color retention between polyesters and fluoropolymers relate both to the base resin and the pigmentation (polyester versus PVDF and organic versus ceramic), and in a study which spans a wide color space, with both systems formulated to the same colors at roughly equal low gloss levels, performance in 45° South Florida exposure is as follows:

COLOR	RESIN SYSTEM	ORIGINAL GLOSS	RETAINED GLOSS (3 YEARS)	ΔE
White	Polyester	30.0	11.7	1.60
White	Kynar 5000 PVDF	37.0	44.7	1.09
Yellow	Polyester	28.0	9.2	15.43
Yellow	Kynar 500⊕ PVDF	15.0	20.7	3.06
Dark Blue	Polyester	29.0	2.7	9.48
Dark Blue	Kynar 500♥ PVDF	4.0	5.5	1.20
Black	Polyester	32.0	2.8	10.30
Black	Kynar 500@ PVDF	17.0	16.9	1.26
Dark Brown	Polyester	38.0	1.7	11.52
Dark Brown	Kynar 500● PVDF	43.0	39.5	1.14

The two systems utilized to perform this study are currently commercial systems which are in wide distribution for architectural applications of the

typical variety (everything from window systems to entryways to spandrel panels to full curtain-wall configurations). Five year exposures in Florida in full strength fluoropolymer powder and liquid systems are virtually indistinguishable in their performance against the requirements for color stability, gloss retention, film integrity and other barometers of performance. In the automotive marketplace, interest has now expanded from the critical fluids tubing application to utilizing PVDF cabling compounds for fuel hoses (both in vehicle and in fuel pumping applications) and to the use of PVDF films for fuel tank lining applications and for body-color-matched side molding applications where the exceptionally strong weathering resistance can support the cost of a more expensive material. There are numerous evaluations underway at the domestic Big Three and the transplants to expand the use of this technology in its more compliant forms (film, powder, water-borne, etc.) as well as in the traditional solvent systems, with the obvious advantages for environmental compliance favoring the non-solvent borne materials.

Before closing, it is appropriate to review other characteristics of fluoropolymer powder coatings technologies which must be kept in mind during its application. As with other powder coatings, this material is melt-processable, and recommended peak metal temperatures must be reached in order to achieve full "cure" of the applied film. The recommended time at temperature is the same as it is for its liquid counterpart (5 minutes above 450°F.). In order to optimize the flow and leveling of the topcoat, the powder primer must be at least partially cured prior to application of the topcoat. This preliminary cure also serves to assure that there will be none of the powder primer which is knocked down into the reclaim of the topcoat, thereby diminishing its integrity. The liquid flash primer requires a minimum of 5 minutes of flash time prior to application of the topcoat to assure that all residual solvents are removed from the primer film and do not blow through the topcoat during the curing cycle. In addition, the liquid flash primer is formulated without the traditional strontium chromate component, making it the most environmentally compliant liquid material currently available.

In the other segments of this conference, many other aspects of the handling and application of thermoplastic powder coatings have been covered. For both the automotive and architectural communities which are still coming to grips with this technology, the opportunity this material presents to set aside all of the potential environmental complications which the traditional technology entails (the need to incinerate at considerable expense, and the calculated risk of chasing federal and local air quality regulations which will be ratcheted down in increments over the next several years during the enforcement of the Clean Air Act) is significant. Given the extremely high level of VOCs existing in the traditional formulations (higher on a per unit basis than almost any other conventional coating), the liquid fluoropolymer coatings will be among the first to be targeted by the probable increase in regulatory enforcement over the next The availability of a proven technology in a fully few months and years. compliant form which exceeds the demands and expectations of the material specifiers, the regulators, and the architectural and automotive customers is a tribute to those who had the foresight to tackle the unique processing characteristics of a performance-capable thermoplastic material, and to develop the appropriate procedures to make it viable.

David M. Grafflin Market Manager - Coatings DEXTER AUTOMOTIVE MATERIALS DIV. psb/5-6-93

NOTE: Kynar 5000 and Kynar 500PC are registered trademarks of Elf Atochem North America, Inc. (formerly the Pennwalt Corporation), for their architectural fluoropolymer resins.

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Currently serving as Market Manager-Coatings for the Coatings Group of Dexter Automotive Materials Division, encompassing the activities of EVODEX Powder Coatings (a joint venture of The Dexter Corporation and Evode Group plc), Mr. Grafflin has spent the last eight years in domestic and international market development of a variety of fluoropolymer technologies, with a particular emphasis in full strength PVDF powder coatings.

Since the commercial introduction of this material in the North American market in 1991 (when it reached five years Florida exposure), EVODEX has provided a full spectrum of powder coatings for interior and exterior residential, commercial, industrial and monumental architectural applications.

SESSION 4

FEDERAL PROGRAMS

PAPERS PRESENTED:

"U.S. Navy Compliance to Shipbuilding and Ship Repair Environmental Regulations"

by

Alex Kaznoff

Naval Sea Systems Command

Arlington, Virginia

"Low-VOC Coatings Developed by DOE for Environmentally Conscious Manufacturers"

by

Mark D. Smith

Allied Signal, Inc.

Kansas City, Missouri

"The Precedent-Setting Use of a Pollution Prevention Project in an EPA Enforcement Settlement: The First Dollar-for-Dollar Penalty Offset"

by

David Nelson

EnviroSearch International

Salt Lake City, Utah

and

James J. Periconi

Donovan Leisure Newton & Irvine

New York, New York

"Army Pollution Prevention Success Stories"

by

Jack Hurd

Army Acquisition Pollution Prevention Support Office

Alexandria, Virginia

and

Mark W. Ingle

Ocean City Research Corporation

Arlington, Virginia

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US NAVY COMPLIANCE TO SHIPBUILDING AND SHIP REPAIR ENVIRONMENTAL REGULATIONS

NAVAL SEA SYSTEMS COMMAND CODE 05M ALEX KAZNOFF

OVERVIEW

- O CLEAN AIR ACT AMENDMENT (CAAA)
- O CONTROL TECHNIQUES GUIDELINES (CTG)
- O NATIONAL EMISSION STANDARD FOR HAZARDOUS AIR POLLUTANTS (NESHAP)
- O CALIFORNIA REGULATIONS
- O CURRENT DOD COMPLIANCE EFFORTS
- O Dod Tri-Service <u>R&D</u> COATINGS PROGRAMS

CLEAN AIR ACT AMENDMENT (CAAA), PUBLIC LAW 101 - 549 - NOVEMBER 15, 1990

O PURPOSE

o AMEND THE CLEAN AIR ACT (CAA) TO PROVIDE FOR ATTAINMENT AND MAINTENANCE OF...

	TITLE	PROVISION
	1	NATIONAL AMBIENT AIR QUALITY STANDARDS (NAAQS)
	2	PROVISIONS RELATING TO MOBILE SOURCES
	3	HAZARDOUS AIR POLLUTANTS (HAPs)
4.4	4	ACID DEPOSITION CONTROL
117	5	PERMITS
-	6	STRATOSPHERIC OZONE PROTECTION
	7	PROVISIONS RELATING TO ENFORCEMENT
	8	MISCELLANEOUS PROVISIONS
	9	CLEAN AIR RESEARCH
	10	DISADVANTAGED BUSINESS CONCERNS
	11	CLEAN AIR EMPLOYMENT TRANSITION ASSISTANCE

*NOTE: TITLES 1 & 3 IMPACT THE MATERIALS USED OR GENERATED IN THE APPLICATION AND REMOVAL OF PAINTS, COATINGS, AND SOLVENTS

CAAA TITLES 1 & 3

- O NAAQS (TITLE 1)
 - OZONE: ESTABLISH AND ISSUE CONTROL TECHNIQUES GUIDELINES (CTGs) TO REDUCE AGGREGATE EMISSIONS OF VOLATILE ORGANIC COMPOUNDS (VOCs)
 - >> <u>YOCs:</u> MANY SOLVENTS USED IN PAINTS CHEMICALLY REACT WITH NOx AND SUNLIGHT IN THE ATMOSPHERE TO FORM OZONE
 - O PM-10: ESTABLISH AND ISSUE CONTROL TECHNIQUES GUIDELINES (CTGs) TO REDUCE AGGREGATE EMISSIONS OF PM-10
 - >> <u>PM-10</u>: PARTICULATE MATTER WITH A DIAMETER OF LESS THAN OR EQUAL TO TEN MICRONS
- O HAPs (TITLE 3)
 - O HAPS: ESTABLISH AND ISSUE NATIONAL EMISSION STANDARD FOR HAZARDOUS AIR POLLUTANTS (NESHAP)
 - >> <u>HAPs</u>: HAZARDOUS AIR POLLUTANTS WHICH POSE ADVERSE ENVIRONMENTAL AND/OR HUMAN HEALTH AND SAFETY EFFECTS (APPROX. 189 HAPs)

CONTROL TECHNIQUES GUIDELINES (CTGs) FOR VOC SOURCES

- O FEDERAL OZONE MEASURES (CAAA TITLE I)
 - O ISSUE CTGS FOR STATIONARY SOURCES OF VOC EMISSIONS FROM PAINTING IN THE FOLLOWING INDUSTRIES:

- AUTOMOBILE/LIGHT TRUCK - METAL FURNITURE

- METAL COIL - LARGE APPLIANCES

- FABRICS - PAPER

- MAGNETIC WIRE INSULATION - CANS

- MISCELLANEOUS METAL PARTS - FLATWOOD PANNELING

AEROSPACE

- * SHIPBUILDING OPERATIONS AND SHIP REPAIR COATINGS AND SOLVENTS COVERS VOC AND PM-10 EMISSIONS
- O HAZARDOUS AIR POLLUTANTS (CAAA TITLE 3)
 - O ISSUE NESHAPS FOR ALL STATIONARY SOURCES THAT EMITS HAPS

SHIPBUILDING OPERATIONS AND SHIP REPAIR CTG

O FEDERAL REGULATORY DEADLINES

ISSUANCE: BEFORE NOVEMBER 15, 1993
EFFECTIVITY: TO BE DETERMINED, FED & STATE IMPLEMENTATION
MAY BE DIFFERENT

O IMPACTS

- EXISTING SHIPBUILDING AND SHIP REPAIR EMISSIONS SOURCES IN NONATTAINMENT AREAS
- VOC AND PM-10 EMISSIONS FROM THE APPLICATION AND REMOVAL OF PAINTS, COATINGS, AND SOLVENTS ABOARD MARINE VESSELS (EXCLUDING PLEASURE CRAFT)
- O VOC AND PM-10 EMISSIONS STANDARDS BASED ON BEST AVAILABLE CONTROL MEASURES (BACM)
 - BACM: AN EMISSION LIMITATION THAT WILL ACHIEVE THE LOWEST ACHIEVEABLE EMISSION RATE FOR THE SOURCE TO WHICH IT IS APPLIED

SHIPBUILDING OPERATIONS AND SHIP REPAIR NESHAP

O FEDERAL REGULATORY DEADLINES - NESHAP

ISSUANCE: NOVEMBER 15, 1993 (ORG. NOV '94)
EFFECTIVITY: TO BE DETERMINED

- O IMPACTS
 - O NEW AND EXISTING SHIPBUILDING AND SHIP REPAIR FACILITIES CONSIDERED MAJOR AND AREA EMISSIONS SOURCES (189 HAPs)
 - MAJOR SOURCE: 10 TONS/YR OR MORE OF ANY HAP OR 25 TONS/YR OR MORE OF ANY COMBINATION OF HAPS
 - PHASE I DEVELOP HAPS EMISSIONS STANDARDS BASED ON MAXIMUM ACHIEVEABLE CONTROL TECHNOLOGY (MACT)
 - MACT: NEW AS STRINGENT AS THE AVG. ACHIEVED BY THE BEST CONTROLLED SIMILAR SOURCE

 EXISTING AS STRINGENT AS THE AVG. ACHIEVED BY THE BEST 12 PERCENT OF EXISTING SOURCES
 - o PHASE II DEVELOP RISK-BASED EMISSION REDUCTIONS

STATE REGULATIONS

- O STATES REQUIRED TO DEVELOP "STATE IMPLEMENTATION PLAN" (SIP) WHICH ADOPTS FEDERAL REQUIREMENTS AS A MINIMUM TO ACHIEVEMENT ATTAINMENT OF CAA
 - o CALIFORNIA
 - 14 AIR QUALITY MANAGEMENT DISTRICTS (AQMDs)
 - ..BAY AREA AQMD
 ..SOUTH COAST AQMD
 ..SAN DIEGO APCD
- O CALIFORNIA REGULATIONS IMPACTING Dod ACTIVITIES
 - o ARCHITECTURAL & INDUSTRIAL MAINTENANCE (AIM) REGULATIONS
 - PAINTS APPLIED TO SHOREBASED FACILITY STRUCTURES
 - MISCELLANEOUS METAL PARTS AND PRODUCTS
 - PAINTS APPLIED TO SMALL METAL PARTS (USUALLY LIMITED TO SHOP APPLICATIONS

CALIFORNIA REGULATIONS IMPACTING DOD ACTIVITIES (cont'd)

- c AEROSPACE COATINGS
 - PAINTS APPLIED TO AIRCRAFT OR EQUIPMENT/ORDNANCE INSTALLED ON AIRCRAFT
- o MARINE COATINGS
 - PAINTS APPLIED TO MARINE VESSELS OR EQUIPMENT/ORDNANCE INSTALLED ABOARD MARINE VESSELS
- O CALIFORNIA REGULATION REQUIREMENTS
 - GENERAL LIMITS FOR VOC CONTENT
 - AIR DRIED COATINGS (CURE AT TEMPERATURES BELOW 194°F)
 - BAKED COATINGS (CURE AT TEMPERATURES ABOVE 194°F)
 - o SPECIAL COATING APPLICATION LIMITS FOR VOC CONTENT (ESSENTIAL FOR CONTINUED MARINE COATINGS OPERATIONS
 - VOC CONTENT LIMITS BASED ON IN-SERVICE ENVIRONMENT AND PERFORMANCE REQUIREMENTS

 ..ANTIFOULING (AF) PAINTS NAVY APPLICATION

 ..CHEMICALAGENT RESISTANT COATINGS (CARC) ARMY APPLICATION

 ..AIRCRAFT WING COATINGS AIR FORCE APPLICATION

NAVY RESPONSE TO CALIFORNIA VOC REGULATIONS

- O REFORMULATED PAINTS AND COATINGS TO COMPLY WITH MARINE COATINGS REGULATIONS
 - o REDUCED SOLVENT (VOC) CONTENT FOR ENVIRONMENTAL COMPLIANCE
 - o ENSURE CONTINUED OPERATIONAL AND SERVICE LIFE PERFORMANCE
 - SUBSTITUTION/CANCELLATION OF PAINTS
- O PURSUE NEW TECHNOLOGIES FOR VOC REDUCTION
 - HIGH SOLIDS PAINTS AND COATINGS
 - O WATER BASED PAINTS
 - POWDER COATINGS (THERMAL PLASTIC)
- O CALIFORNIA COMPLIANCE PROGRAM
 - O THREE YEAR PROGRAM (\$3M) TO DEVELOP, TEST, AND QUALIFY REPLACEMENT NAVY MARINE COMPLIANT PAINTS

NAVY "CALIFORNIA COMPLIANCE" LESSONS LEARNED

- O LEAD TIMES (BEST & WORST CASE: 24 VS 45 MONTHS)
 - o TEST & EVALUATION (T&E): TECHNICAL DIFFICULTIES IN R&D IMPACTS
 COMPLIANCE SCHEDULE
 - LABORATORY REFORMULATION
 - PERFORMANCE VALIDATION
 - TOXICOLOGICAL/HAZMAT REVIEW-ATMOSPHERIC CONTROL TESTING
 - SPECIAL APPLICATION TESTING (i.e. FIRE AND/OR HEAT RESISTANCE)
 - DOCUMENTATION/SPECIFICATION UPDATE
 - QUALIFICATION OF VENDOR PRODUCTS
 - TECHNICAL GUIDANCE FOR END USER (FLEET)
 - REVISION OF SPECIFICATIONS TO INCLUDE APPROVED PRODUCTS
 - **O** IMPLEMENTATION OF COMPLIANT MATERIAL TO FLEET
 - < < EXPERIENCED SIGNIFICANT LOGISTICS PROBLEMS AND DELAYS > >
 - NEW PROCUREMENT OF COMPLIANT MATERIAL (CONTRACT BUYS & NATIONAL STOCK NUMBERS (NSNs)
 - COMPETITIVE BUYS SHIPMENT/DISTRIBUTION
 - STOCKING AND SUPPLY TRANSITION OF COMPLIANT MATERIAL TO THE SUPPLY SYSTEM

NAVY LESSONS LEARNED (cont'd)

- O INTERIM VARIANCES NEGOTIATED IN ALL THREE DISTRICTS TO ALLOW STOCKING AND SUPPLY
- O NAVY STILL COMPLETING UPDATE TO NAVAL SHIPS TECH MANUAL (NSTM CHAPTER 631) AND SPECIFICATIONS TO REFLECT CHANGES
- O NAVY NOW IN COMPLIANCE WITH SEPTEMBER 1991 RULE AND SEPTEMBER 1994 PENDING RULE
- O SPECIALTY CATEGORIES MUST BE SPECIFIED TO ENSURE THE CONTINUED USE OF CURRENT NAVY COATINGS

CURRENT NAVY COATINGS PROGRAM EFFORTS

- O REFORMULATE SHIPBOARD PAINTS AND COATINGS TO REDUCE VOC CONTENT LIMITS TO THE LOWEST PRACTICAL LEVELS
 - o SUPERCRITICAL CO, TECHNOLOGY
- O SHIPBOARD PAINTS AND COATINGS HAZARDOUS MATERIALS DATABASE
 - o ENVIRONMENTAL ISSUES
 - IDENTIFY HAPS LEVELS IN ALL NAVY SHIPBOARDS PAINTS AND COATINGS
 - .. REFORMULATE PAINTS TO SUBSTITUTE/ELIMINATE HAPS TO COMPLY WITH STATE AND PENDING EPA LEGISLATION
 - HEALTH AND SAFETY ISSUES
 - IDENTIFY HEAVY METALS CONTENT IN PAINTS IN EXCESS OF PERMISSABLE LIMITS
 - IDENTIFY IMPROVED PAINT REMOVAL EQUIPMENT AND TECHNOLOGY TO MINIMIZE POTENTIAL HEALTH HAZARDOUS DURING COATING OPERATIONS

ARMY COATINGS PROGRAM

- O REFORMULATED PAINTS AND TOPCOATS TO MEET CALIFORNIA VOC LIMITS
 - o PRIMERS
 - o TOPCOATS
 - CARC COATINGS
- O CURRENT R&D ACTIONS
 - REFORMULATION OF LAQUERS
 - o AMMUNITION ENAMEL
 - o HEAT RESISTANT COATINGS
- O EXPANDING USE OF POWDER COATINGS
- O EXPANDING USE OF ELECTROSTATIC COATINGS

AIR FORCE COATINGS PROGRAM

- O CURRENTLY IN COMPLIANCE WITH CALIFORNIA AEROSPACE COATINGS REGULATION PRIMERS AND TOPCOATS
 - o AIRCRAFT
 - o WEAPON SYSTEMS
 - GROUND SUPPORT EQUIPMENT
- O AIR FORCE DEPENDS HEAVILY ON AEROSPACE INDUSTRY FOR R&D OF AEROSPACE PAINTS AND COATINGS FOR ENVIRONMENTAL COMPLIANCE
- O REQUIRES R&D COATINGS DEVELOPMENT
 - FUEL TANK COATINGS
 - ADHESIVE STRUCTURAL BONDING PRIMER
- O NO REPLACEMENT FOR CHROMIUM (VI) FOR USE IN ANTICORROSIVE PRIMERS

ANALYSIS OF PROPOSED CTG FOR MARINE COATINGS

- O PROPOSED EPA CTG VASTLY DIFFERENT FROM CALIFORNIA MARINE COATING REGULATIONS
 - O ALL MARINE COATINGS APPEAR TO BE GROUPED INTO FOUR CATEGORIES BASED UPON CHEMISTRY AS OPPOSED TO APPLICATION
 - ALKYD PAINT SYSTEMS
 - EPOXY PAINT SYSTEMS
 - INORGANIC ZINC PAINTS
 - ANTI-FOULING PAINTS

**NOTE: THIS MEANS OF CLASSIFICATION DOES NOT CONSIDER MEANS OF APPLICATION OR INTENDED SERVICE OF THE PAINT WHICH DICTATES VOC CONTENT AND MAY VARY GREATLY

- O EPA PROPOSED CTG IS NOT CLEAR AS TO WHAT DISPENSATION WILL BE GIVEN TO SPECIAL APPLICATION COATINGS (i.e., POLYURETHANES, HIGH SOLIDS ALUMINUM HEAT RESISTANT PAINTS, etc...)
- O EPA PROPOSED CTG IS LIKELY TO ADOPT CALIFORNIA '94 VOC LIMITS
 - o GENERAL COATING VOC CONTENT LIMIT 340g/I (AIR DRIED COATINGS)

ANALYSIS OF PROPOSED NESHAP FOR MARINE COATINGS

- O EPA NESHAP
 - O REGULATES 189 HAPS EMITTED DURING SHIPBUILDING OPERATIONS AND SHIP REPAIR
 - HAPS LIMITS AND TECHNICAL APPROACH ARE UNKNOWN AT THIS TIME
 - * NAVY CONCERN THAT EPA WILL REGULATE LOW HAPS AND LOW VOC WHICH MAY NOT BE TECHNICALLY FEASIBLE FROM AN APPLICATION AND PERFORMANCE STANDPOINT
- O CALIFORNIA HAPS REGULATIONS
 - AIR TOXICS "HOT SPOTS" INFORMATION AND ASSESSMENT ACT OF 1987
 - REGULATES APPROXIMATELY 740 HAPs (INCLUDING 189 EPA HAPs)
 - HAPs ARE GROUPED FOR INVENTORY REPORTING
 - ...QUANTIFY EMISSIONS OF APPROXIMATELY 400 HAPS
 - ..DOCUMENT PRESENCE OF APPROXIMATELY 340 HAPS

Dod Tri-Service R&D Coatings Programs

- O TRI-SERVICE ENVIRONMENTAL QUALITY STRATEGIC PLAN PROGRAM (GREEN BOOK)
 - O DOD PILLAR 3: POLLUTION PREVENTION
 RELIANCE SUBAREA: COATINGS APPLICATION AND REMOVAL
 REQUIREMENT THRUST 3B: PAINT STRIPPING AND COATINGS
- O GOAL:
 - PRESERVE THE ENVIRONMENT
 - o MINIMIZE TOXIC OR HAZARDOUS MATERIALS USED AND/OR GENERATED
 - ELIMINATE POTENTIAL FINES
 - o IMPROVE HUMAN HEALTH AND SAFETY
 - **REDUCE REGULATORY REPORTING BURDEN**
 - o REDUCE DISPOSAL, EQUIPMENT, AND CONTROL COSTS
- O PROVIDES R&D TECHNOLOGIES IN THE AREAS OF:
 - ALTERNATIVE PAINTING AND STRIPPING METHODS
 - REFORMULATION OF PAINTS AND STRIPPERS
 - IMPROVED APPLICATION, CLEANING, AND STRIPPING EQUIPMENT
 - IMPROVED ABRASIVE BLASTING EQUIPMENT AND RECOVERY/RECYCLING/TREATMENT EQUIPMENT

DoD COATINGS RESEARCH PROGRAMS

- O NON-HAZARDOUS CORROSION PROTECTION PAINTS AND COATINGS NAVY
- O NON-HAZARDOUS ANTIFOULING/FOULING RELEASE HULL COATINGS NAVY
- O ELIMINATE CHROMATE WASTE GENERATION FROM CORROSION PROTECTION PROCESSES ARMY, NAVY, AIR FORCE
- O REDUCE HAZARDOUS WASTE FROM PAINT CONTAINER DISPOSAL ARMY, NAVY
- O NON-HAZARDOUS CHEMICAL AGENT RESISTANT COATINGS ARMY
- O REUSE/RECYCLE PAINT SLUDGE AND FILTERS ARMY
- O COST-EFFECTIVE NON-POLLUTING PAINT STRIPPING METHODS ARMY, NAVY, AIR FORCE
- O NON-POLLUTING, LOW-VOC CHEMICAL STRIPPERS ARMY, NAVY, AIR FORCE
- O IMPROVED BLAST GRIT RECYCLING TECHNOLOGY NAVY, AIR FORCE

DoD COATINGS RESEARCH PROGRAMS (cont'd)

- O REDUCE HAZARDOUS WASTE GENERATION FROM PLASTIC MEDIA BLASTING AIR FORCE
- O ELIMINATE CHROMATE WASTE GENERATION FORM PAINT STRIPPING PROCESS ARMY, AIR FORCE
- O REDUCE HAZARDOUS WASTE GENERATION FROM CHEMICAL PAINT STRIPPING OPERATIONS ARMY, AIR FORCE
- O DEVELOP ENVIRONMENTALLY SAFE PAINT STRIPPING OPERATION FOR SMALL PARTS AIR FORCE
- O TECHNOLOGY TO RECYCLE/REUSE PAINT-REMOVAL MEDIA ARMY, AIR FORCE
- O MINIMIZATION OF WASTE FROM LEAD BASED PAINT (LBP) DEBRIS ARMY, AIR FORCE
- O MODELS/THEORIES FOR IMPROVED CORROSION CONTROL NAVY, AIR FORCE

R&D COST AND FUNDING ESTIMATES

O COST ESTIMATES: TECH. BASE TECH. DEMO IMPLEMENTATION TOTAL \$6,670K \$40,769K \$0K \$47,439K

O FUNDING PROFILE:

	<u>FY93</u>	FY94	FY95	FY96	FY97	FY98	FY99
ARMY	300	490	500	300	300	300	205
NAVY	1650	5000	8300	8260	4575	1350	690
AIR FORCE	1100	600	675	1800	2250	1460	539
TOTAL	3050	6090	9475	10360	7125	3110	1434
UNFUNDED	<u>3150</u>	970	<u>1360</u>	<u>1015</u>	300	0	0
TOTAL	6200	7060	10835	11375	7425	3110	1434

NAVAL SEA SYSTEMS COMMAND (CODE 05M1) PAINTS (per NAVAL SHIPS' TECHNICAL MANUAL - CHAPTER 631 OF 11/01/92)

NONCOMPLIANT PAINT	COMPLIANT ALTERNATIVE
TT-E-490	MIL-E-24365
MIL-P-24441	MIL-P-24441C
MIL-P-15930, F120	MIL-P-24441C, F150
DOD-E-1115C, F30	NUCLEAR APPLICATION:
	DOD-E-1115C, F30
	NON-NUCLEAR APPL:
•	DOD-C-24596 OR NAVY F25A
DOD-E-18210	DOD-C-24596 OR NAVY F25A
DOD-E-18214	DOD-C-24596 OR NAVY F25A
DOD-E-698	DOD-C-24596 OR NAVY F25A
DOD-E-699	MIL-E-24635
DOD-E-700	NUCLEAR APPLICATION:
	MIL-E-15090, F111
	NON-NUCLEAR APPL:
	DOD-C-24596 OR NAVY F25A
DOD-P-15146	MIL-E-24635
DOD-P-15183	MIL-E-24635
MIL-E-15090, F111	NUCLEAR APPLICATION:
	MIL-E-15090, F111
	NON-NUCLEAR APPL:
	DOD-C-24596 OR NAVY F25A
MIL-E-5556	MIL-E-24635
DOD-P-24631	DOD-P-24631B
RABLI FLAA 1 (64 104 104 104 104 104 104 104 104 104 10	

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NAVAL SEA SYSTEMS COMMAND (CODE 05M1) PAINTS (cont'd) (per NAVAL SHIPS' TECHNICAL MANUAL - CHAPTER 631 OF 11/01/92)

NONCOMPLIANT PAINT COMPLIANT ALTERNATIVE
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DOD-E-24607	DOD-E-24607B
DOD-C-24667	DOD-C-24667
DOD-P-23236	DOD-P-23236
TT-P-28	TT-P-28 (LOW VOC)
TT-P-645	
MIL-P-24647	MIL-P-24647
MIL-P-15931	MIL-P-15931
MIL-D-23003	MiL-D-23003
DOD-P-24648	DOD-P-24648
MIL-D-24483	MIL-D-24483
TT-E-489	
	LOCAL PURCHACE OF
	LOW YOC MATERIAL
DOD-P-15328	TT-P-645B, F84 OR
	MIL-P-24441C, F150
TT-P-1757	TT-P-645B, F84 OR
	MIL-P-24441C, F150
TT-P-641	TT-P-645B, F84 OR
	MIL-P-24441C, F150
TT-S-711	LOCAL PURCHACE OF
	LOW VOC MATERIAL
TT-V-119	LOCAL PURCHACE OF
	LOW VOC MATERIAL

NAVAL SEA SYSTEMS COMMAND (CODE 05M1) PAINTS (cont'd) (per NAVAL SHIPS' TECHNICAL MANUAL - CHAPTER 631 OF 11/01/92)

NONCOMPLIANT PAINT	COMPLIANT ALTERNATIVE
MIL-C-46081	MIL-C-46081
MIL-P-24555	TT-P-28 (LOW VOC)
DOD-C-24596	
MIL-C-24380	MilC-24380

Low-VOC Coatings for ECM

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(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

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AGENDA

PAINTS

- Environmental concerns
- Compliance actions
- Current paint status
- Anticipated future work
- UV coatings

DRY FILM LUBRICANTS

- Environmental concerns
- Replacement actions





AIR POLLUTION REGULATION

- Missouri Air Pollution Rule 10 CSR 10-2.230, Control of Emissions from Industrial Surface Coating Operations
- Applies to locations emitting more than 6.8
 kilograms per day or 2.7 tons per year
- KCP regulated under the provisions for painting "Miscellaneous Metal Parts"
- Emission Limit of 3.5 pounds of VOC's per gallon of coating as applied
- Effective date of Compliance; December 31, 1982





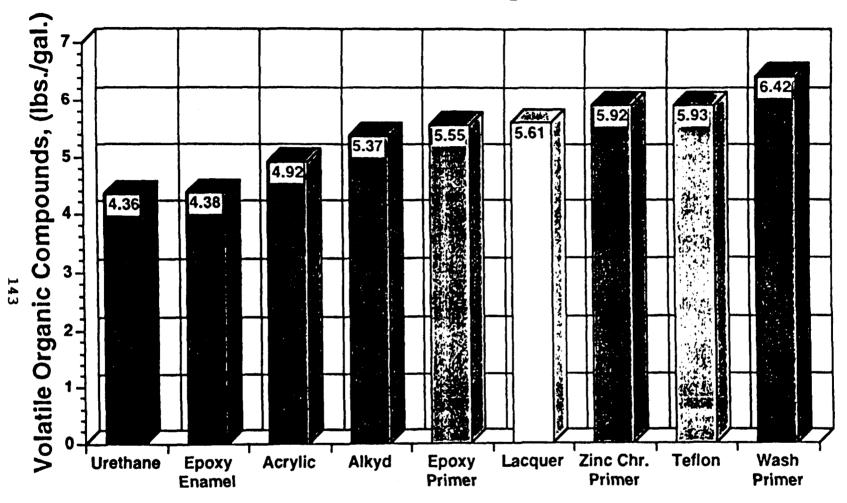
COMPLIANCE ACTIONS:

- Spray painting operations voluntarily halted
- Began process of developing "site plan" and obtaining state and local EPA approval
- Started VOC survey of currently used paints and began search for "compliant" replacement paints





VOC's of Selected High VOC Paints



Paint Systems





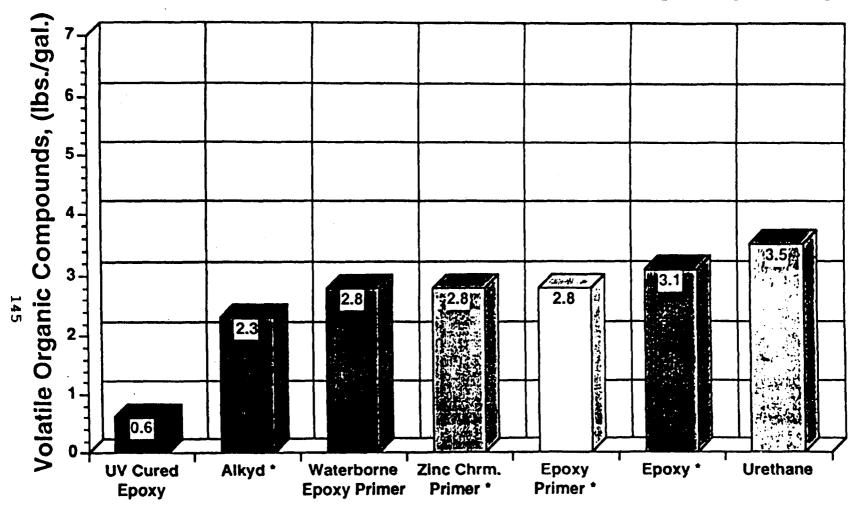
COMPLIANCE ACTIONS: (continued)

- Started survey of painting industry contacts to determine possible alternate sources of production painting
- Obtained and installed activated carbon filtering
 - systems for production painting area
- Began obtaining and VOC-testing replacement paints





VOC's of Selected Low VOC Paints



Paint Systems





AREAS OF CONCERN IN SWITCHING TO REPLACEMENT PAINTS

- Customer requirements for color, corrosion protection and durability
- Maintaining Military Specifications as basis for production paints
- Compliant paints using "exempt" chlorinated
 solvents
- Coatings for which there were no direct replacements, (lacquers, Teflon® paints, wash primers, dry film lubricants)
- New paint techniques and equipment that might be necessary





PRESENT PAINTING STATUS

- Almost all applications using low VOC paints
- Limited use of high VOC materials within special booth, stack emissions routed through activated carbon filters until alternates found
- Significantly reduced number of routinely used different paint systems (from 25 down to approximately 5)
- Larger percentage of paints based on Military Specifications and Federal Standard Color numbers
- Significantly reduced VOC emissions





ANTICIPATED FUTURE PAINT WORK

- Continued emphasis on high-solids, low VOC polyurethane and alkyd enamel paints
- Reduction or elimination of chlorinated solvent-based coatings
- Investigation of new lead and chromate-free Military
- **Specification primers**
- Elimination of special booth and/or filtration of all booths
- Evaluation of alternative coating methods





ALTERNATIVE METHODS INVESTIGATIONS

- A study on powder coating is underway.
- New powder coating booth and two new powder coating guns are installed and operational.
- Electrophoretic coatings are being studied. New equipment is being obtained and set-up.
- Alternate cleaning and pretreatment methods are being studied, (alternate solvents, aqueous cleaning, dry plasma cleaning, chromate conversion replacements).





UV CURABLE COATINGS

- The materials are essentially 100% solids and therefore have a very low VOC content.
- The materials are very quick curing thus increasing through-put and decreasing chances for surface defects.
- Special curing equipment is required; curing of the material is line-of-sight from the UV lamps.
- Clear or translucent materials work best; opaque/pigmented materials are limited in curing by their ability to absorb UV within the bulk of the coating.



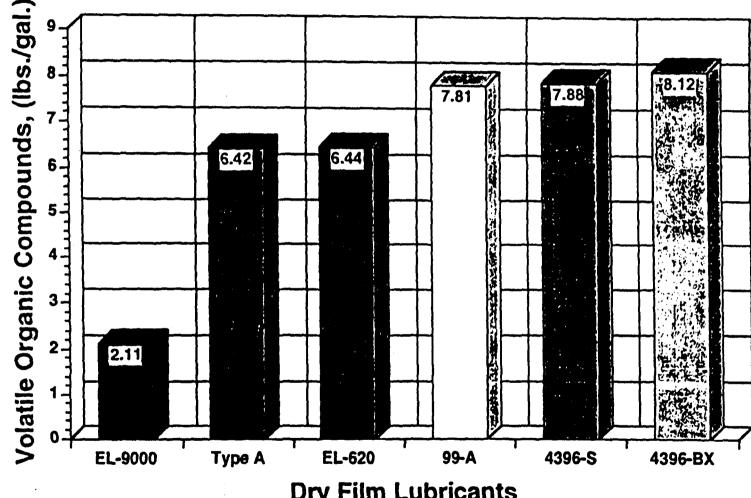


DRY FILM LUBRICANTS

- Under current Missouri regulations regarding emissions from "surface coating operations", dry film lubricants are not included
- Most of the presently used materials are high VOC,
 from 6.42 to 8.12 pounds per gallon applied
- Division goal of reducing emissions to "as low as reasonably attainable" is driving substantial investigation into low VOC dry film lubricant technologies











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AREAS OF CONCERN IN SWITCHING TO REPLACEMENT DRY FILMS

- Application techniques and equipment will most likely require substantial changes. (Licensing of some technologies may be required.)
- Performance requirements of the present materials are not well defined, therefore proper replacements will be hard to define.
- New low VOC versions of existing dry film lubricants are relatively unproven in actual use which causes some trepidation in adopting their use.





LOW VOC DRY FILM ACTIONS

- A group is studying dry film lubricants, surveying the dry film market and attempting to define performance requirements for their use.
- Possible alternatives include: Dicronite®, Microseal®, sputtering, sputter/ion treatment, electrophoretic coatings, increased hardness coatings, and E/M's new low VOC materials
- Study will determine objective inspection techniques for dry films
- Several other small short term tests are being made on individual parts or assemblies





SUMMARY

- Environmental concerns about surface coating operations prompted an analysis of coatings materials and other compliance actions.
- The painting operations equipment underwent some modifications within the approved site plan.
- The switch to low VOC paints was made as soon and as completely as possible within certain constraints.





SUMMARY (continued)

- Changes in the type of dry film lubricants used are anticipated.
- Other low VOC painting techniques such as dry powder, electrophoresis and UV coatings are being investigated.
- Investigations continue regarding other environmental concerns such as chlorinated solvent and hexavalent chrome reduction.





(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

The Precedent-Setting Use of a Pollution Prevention Project in an EPA

Enforcement Settlement: The First Dollar-for-Dollar Penalty Offset

Presented by:

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ABSTRACT

Prior to the case described in this paper, the U.S. Environmental Protection Agency had not allowed an environmental project dollar-for-dollar setoff against a proposed fine in an enforcement action. Typical penalty offsets were historically in the range of 15 to 25% at the time of this settlement, although dollar-for-dollar setoffs were theoretically available. Relatively few projects of this nature had been negotiated with regulatory agencies, and virtually none in a RCRA enforcement action. This pollution prevention Supplemental Environmental Project (SEP) is one of five types of projects allowed by the new EPA policy on the use of SEPs in enforcement actions. This paper describes the development of the legal and technical strategy utilized by the authors to aid the client in its settlement approach to Region IX EPA. Finally, the results of the implementation of the project to the company are discussed and the conclusion is made that this multi-media pollution prevention project foreshadows a significant developing state and federal regulatory trend.

DESCRIPTION OF THE FACILITY AND PROCESSES

The described facility, located in an industrialized area of San Leandro,
California, is an office furniture manufacturing company employing 65 full-time
workers in two shifts. As was true in early 1991, when the enforcement inspection
discussed in this paper took place, the business utilizes bulk materials such as sheet and
coil metals which are in turn bent, welded, assembled and painted to specifications.
Primary products are storage cabinets, bookcases, and shelving.

After metal forming occurs, the steel parts are attached to an overhead conveyor line which runs through a chemical spray rinse system. These rinses remove cutting oils from the parts as well as coat the semi-finished steel with rust inhibitors. The final rinse consists of a water bath, the effluent of which is discharged via a permit to a Publicly Owned Treatment Works (POTW). The parts, still conveyed via the overhead

line, pass through a large drying oven just prior to entry into the Ransburg automatic spraying mechanism which utilizes an electrostatic application to maximize adherence of the paint to the steel parts. Overspray is collected in air filters which mostly surround the circular paint booths. Remaining overspray adheres to walls, floors and various equipment surrounding the spray system.

While the Ransburg coats a large percentage of the steel parts, they must be finished via hand-held spray guns, operated only by the night shift. Custom furniture not handled by the automatic conveyor system is hand painted in dedicated, three-walled paint booths, the overspray of which is handled via filters. The facility uses Thermal Setting Resin (TSR) paint which requires that painted parts, unlike evaporative formulas, be returned to the drying oven for curing at 350 degrees Fahrenheit. Oven air emissions from the curing process are regulated via a permit.

To understand fully the pollution prevention opportunities this company could and did realize, it is important to note that the company offers custom colors on its products to retail customers at no additional charge and with rapid turnaround. This will be discussed later with regard to its implications in the facility's waste management practices.

DESCRIPTION OF THE ENFORCEMENT ACTION

The facility had a joint enforcement inspection in 1991 by the California

Department of Health Services (now California Environmental Protection Agency) as
well as by EPA, with the federal government eventually exerting jurisdiction (In Matter
of Harbor Universal, Inc., Docket No. RCRA-09-92-0001, U.S. Environmental

Protection Agency, Region IX). The EPA found that the facility had baked paint and
solvent wastes in its drying ovens, which, according to EPA, made the facility an
unpermitted Treatment, Storage or Disposal (TSD) facility subject to regulation under
the Resource Conservation and Recovery Act (RCRA). Region IX issued a

Compliance Order requiring the facility to submit a RCRA Closure Plan for the oven, to submit a plan for immediate compliance with all applicable regulations and to pay penalties of \$341,000.

BACKGROUND ON SUPPLEMENTAL ENVIRONMENTAL PROJECTS (SEPS)

The encouragement by EPA to use SEPs in enforcement proceedings is a natural outgrowth of the overall importance of the pollution prevention emphasis the agency began to apply in the early 1990's following the enactment of the Pollution Prevention Act of 1990. See EPA's Pollution Prevention Strategy, 56 Fed. Reg. 7849 (2/25/91). This new emphasis represented a shift away from "end of the pipe" control strategies which, in EPA's judgment, merely shifted contaminants from one medium (e.g., hazardous waste storage drums on site) to another (e.g., a landfill where the wastes were disposed, or the atmosphere to which incinerated wastes were discharged).

Much of industry, particularly larger companies, had begun, by the mid-80's, to realize the limited value of "end of the pipe" control strategies as the costs of hazardous waste disposal began to skyrocket. Early source reduction strategies in the organic chemical industry, for example, are described in the prescient 1985 study by INFORM, a non-profit, New York-based research organization, entitled <u>Cutting Chemical Wastes</u>, which has recently been updated in a work (<u>Environmental Dividends: Cutting More Chemical Wastes</u> 1992) that demonstrates that enormous progress has been made in corporate attitudes to pollution prevention as well as in actual source reduction. Also fueling this attention and focus was the then new annual rite of Toxic Release Inventory (TRI) data, which showed in 1988, for example, that reporting facilities released 4.57 billion pounds of contaminants directly into the environment.

Under Carol Browner's leadership, the agency is likely to increase the use of SEPS, especially pollution prevention-based SEPs. In fact, the Clinton Administration

early on announced its intention to increase their use and although already found in as many as one in ten negotiated settlements, growth in their use is expected to continue.

In the second of EPA's 1991 Enforcement Policies discussed below, EPA targeted the reduction of 17 high risk chemicals, choosing those offering the best opportunities for source reduction (applicability to the referenced facility discussed later). The overall goal of EPA as of early 1991 was to reduce the total releases of these chemicals by 33% by the end of 1992. (The authors are unaware as to whether EPA believes it has met this goal; however, reductions are believed to have been significant.)

EPA's Regions and program branches are to "investigate flexible, cost-effective regulatory approaches that avoid prescriptive approaches and that rely on market-based incentives...", (EPA Pollution Prevention Strategy, pg.10). EPA is also to "ensure that its enforcement program seeks pollution prevention opportunities as part of ensuring compliance" with environmental laws. "EPA will encourage the inclusion of pollution prevention conditions in Agency enforcement settlements." As noted, the SEPs are, in fact, increasingly employed in negotiated settlements, with pollution prevention SEPs in the lead. The strategy is to "incorporate prevention into every aspect of the Agency's operations in program and regional offices."

The enforcement-related side of this policy is developed in two EPA guidances:

- 1. "EPA's Policy on the Use of Supplemental Environmental Projects (SEPs) in Enforcement Agreements" (2/12/91) defines those projects, other than those required to correct the underlying violation, which a defendant or respondent in administrative proceedings "may undertake in exchange for a reduction in the amount of the assessed civil penalty". Acceptable projects include:
- i. <u>Pollution Prevention Project</u>: one that "substantially reduces or prevents the generation or creation of pollutants through use reduction (i.e., by changing

industrial processes, or by substituting different fuels or materials) or through application of closed-loop processes";

- ii. <u>Pollution Reduction Project</u>: one that "goes substantially beyond compliance with discharge limitations to further reduce the amount of pollution that would otherwise be discharged into the environment...[e.g.] that reduces the discharge of pollutants through more effective end-of-pipe or stack removal technologies; through improved operation and maintenance; or recycling of residuals at the end of the pipe."
- iii. <u>Environmental Restoration Project</u>: one that remediates adverse public health or environmental consequences, "to enhance the environment in the vicinity of the violating facility."
- iv. Environmental Auditing Project: not one "that represents general good business practices," though it may be considered by EPA "if the defendant/respondent undertakes additional auditing practices designed to seek corrections to existing management and/or environmental practices whose deficiencies appear to be contributing to recurring or potential violations."
- v. Public Awareness Project: one that includes publications, broadcasts, or seminars or "which underscore[s] for the regulated community the importance of complying with environmental laws or disseminate[s] technical information about the means of complying with environmental laws," including sponsoring industry-wide seminars. For those considering this SEP option, it is important to note that the project must be publicly advertised as being part of a consent agreement with the EPA in satisfaction of an environmental violation.

Importantly, there must also be a "nexus" or relationship between the original violation and the supplemental project. A vertical nexus exists when the project reduces pollutant loadings to a given environmental medium to offset earlier excess loadings of the same pollutant to the same medium. A horizontal nexus is described as when the project either gives 1) relief for different media at a given facility or 2) relief

for the same medium at different facilities. All SEPs must significantly reduce the total risk posed to public health or the environment by violations. Additionally, all SEPs must be "directly related to addressing compliance problems within the industry within which the violation took place."

While EPA will not generally allow a SEP to be merely a sound business practice that a facility should do anyway (e.g. a basic environmental auditing program), the agency makes an exception in the case of pollution prevention projects alone. The reason is the pollution prevention projects in particular among SEPs have the "advantage of potentially providing significant long-term environmental and health benefits to the public," as well as also being a sound business practice.

Similarly, pollution prevention SEPs can also (unlike other SEPs) include studies which "will be eligible for a penalty offset when they are part of an Agency-approved set of pollution prevention activities at a facility and are designed to correct the violation..." The goal is to encourage pollution prevention studies needed to determine appropriate measures. The "size of the penalty offset may include the costs of the study." Finally, the amount the fine is lowered can reflect the actual dollar expenditures for SEPs, but by no "more than the after-tax amount the violator spends on the project." However, new equipment may be depreciated as a business expense.

2. The second importance guidance, issued the same month as the first guidance and the same day as EPA's Pollution Prevention Strategy, is EPA's "Interim Policy on the Inclusion of Pollution Prevention and Recycling Provisions in Enforcement Settlements" (2/25/91). This policy is intended to be used specifically for those cases where a pollution prevention program will be part of an enforcement settlement. It is this document that contains the list of 17 chemical wastes which EPA has targeted for reduction. Additionally, the policy describes "good faith" as a factor in the settlement: "(t)he willingness of a respondent to correct the violation via a pollution prevention project can be one of the assessment factors used to adjust the

'gravity' component of the penalty." "Voluntary" and "timely" disclosure of the offense may also be taken into account in the final settlement.

At the time of the agency negotiations regarding this enforcement action, in late 1991, SEPs had been used sparingly, and in fact, EPA's (new at the time) Pollution Prevention Information Clearinghouse (PPIC), tasked with recording all SEPs from the various EPA Regional offices, headquarters and states, knew about only four SEP settlements. Used mostly in TSCA, EPCRA, and FIFRA cases up to that point, the reduction in fines were on the order of only 10 to 25% of the amount spent on the pollution prevention project.

Since that time, SEPs have seen widespread use, and are currently estimated by EPA, as noted earlier, to be used in one in ten enforcement cases and growing. EPA's 1992 National Penalty Report, released in the late spring of 1993, indicates there were 409 SEPs negotiated in all programs during 1992. The agency estimated their dollar value at \$50.1 million (though the figure has met with considerable controversy as being too high or too low), with EPA Regions reporting 222 SEPs. The mobile sources air program added 187 SEPs, of which 183 were public awareness projects. More than half of the regional SEPs were pollution prevention projects with TSCA or EPCRA cases comprising 40% of the total. The authors believe many of these settlements arose from "paperwork" reviews such as failures to file Pre-manufacture Notices (PMNs), or Form Rs, respectively, and not the result of investigation-intensive inspections (especially RCRA inspections) conducted by state or federal agencies. According to EPA, programs other than mobile sources, TSCA and EPCRA - e.g., RCRA - each generated no more than 5% of such cases.

DEVELOPMENT OF LEGAL/TECHNICAL STRATEGY

The attorney/consultant team was led by the authors, whose backgrounds were ideally suited for this particular case. Prior to entering private practice, Mr. Periconi

had been an Assistant Attorney General in the Environmental Protection Bureau of the New York Attorney General's office for five years in the early to mid-1980's prosecuting early criminal as well as civil hazardous waste, air, water and wetlands violations; subsequently, he was Chief of the Hazardous Waste Enforcement Bureau for the New York State Department of Environmental Conservation. Prior to starting his consulting firm in 1985, Mr. Nelson was a former multi-program enforcement officer for several regulatory agencies in the State of Utah and served on several EPA oversight committees tasked with reviewing the implementation of RCRA and CERCLA in the early 1980's. While with the agencies, Mr. Nelson was involved with several high profile enforcement cases.

This background allowed the team to realize immediately the severity of the enforcement action both on the face of the allegations and in early conversations with agency personnel, but also the opportunities the company could realize by a substantial program aimed at not only addressing EPA's immediate concerns, but also going far beyond the enforcement action. Our ultimate goal was not only to keep penalties low while satisfying satisfy the agencies, but to help the company turn its overall environmental management program into a cutting-edge business advantage by reducing its production costs.

The initial step was to evaluate the operational as well as strictly environmental aspects of the facility in a broad, unrestricted sense, without emphasizing the enforcement action. In other words, the team was not focused on the hazardous waste paint-baking episodes, as the correction of this problem was obvious, namely, stop the practice and undertake RCRA closure; rather it looked at the facility as a whole, all the time seeking pollution prevention opportunities that would be incorporated eventually into the plan as well as the day-today business activities of the facility.

While facility personnel had a basic understanding of the regulations, and was striving to meet regulatory requirements, it was apparent that the waste handling

practices were grossly inefficient to the point that it was a clear financial burden, enforcement and penalty issues aside. Major waste streams consisted of a great deal of paint overspray over large portions of the painting rooms and surrounding environs, necessitating the use of large quantities of thinner for cleanup. Additionally, paint and solvent contaminated rags were overly abundant as were discardable paint filters, often used well beyond their effective use to the point of over-saturation. To attempt to control the large amount of paint overspray on the floor, large quantities of cardboard were placed on the floor, sometimes layers deep, typically well saturated with paint and therefore quite heavy. This waste material was shipped off to a TSD in pallets, priced by its weight, as an expensive hazardous waste.

Additionally, large quantities of waste paint thinner were generated from cleaning of guns, lines and other miscellaneous chores. While much of this was reclaimed by the company to which the facility sent these wastes, those wastes with a higher proportion of waste paint to solvent could not be reclaimed. Interestingly, the facility also generated enormous amounts of thinner waste due to its marketing success in offering custom colors to clients. The result of this successful marketing effort was, however, the very frequent changing of colors, including the entire flushing of long lines thick with paint. This created, of course, an externality not charged to customers in higher prices for custom lines of products.

Additional potential environmental pollutants, which were reviewed as part of the waste minimization audit, were rinse bath chemical additives from the wastewater stream discharged to the POTW, via permit, as well as the paint solvent emissions in stack gases from the drying ovens, also regulated by a permit. Both permits were current for both emissions; however, the team looked at pollution prevention opportunities with these wastes as well.

Readers familiar with the pioneering work of eminent pollution prevention researchers Joel Hirschhorn, Ph.D. (Hirschhorn & Assoc., Washington D.C.) and

Robert Pojasek Ph.D. (GEI Consultants, Boston, Mass.) know that non-technical barriers, sometimes called "soft" or behavioral barriers, predominantly exist within a facility, the result of which is the typical creation of substantial disincentives for pollution prevention opportunities. In other words, the greatest gains for pollution prevention opportunities are not necessarily or even typically found in high-tech, capital-intensive, R&D solutions; rather they exist in recognizing, modifying, empowering and rewarding facility personnel behavior that precludes the generation of unnecessary amounts of waste. The employees are closest to the problems, and therefore, closest to the most cost-effective, low-tech solutions. It often requires, however, an independent review by outside expert consultants, to identify these industrially dysfunctional, competetively-disadvantaged behaviors. This facility was no different than most others we have consulted to and in this regard, we noted the following during our review:

- Communication barriers were significant between management and workers and were further hampered to a significant degree by language barriers;
- Employees were not empowered nor rewarded to bring forth solutions to the facility's daunting environmental problems;
- Plant engineers and senior managers were convinced that they had investigated every possibility for waste minimization and that no possibilities existed to realize further benefits:
- The night shift posed the greatest threats to the environmental health and safety (EHS) programs. This was due to the fact that no programs existed to sensitize, empower, train and reward (particularly) night shift personnel (nor did they exist to a large degree for the day shift) in solving these problems. Thus, they festered, and ironically presented each new day shift with an ever-increasing, downward spiraling environmental, health and safety headache. The day shift, almost entirely out of touch

with the night shift regarding EHS matters, inherited on a daily basis problems seemingly with no end.

- Pollution prevention opportunities were so apparent and numerous that the prevailing attitudes by all personnel virtually precluded them from seeing them.

These barriers were by far the biggest hurdle to overcome in developing an entirely different environmental, health and safety corporate ethic. Once this was accomplished, with the direct and sincere involvement of the company CEO, sometimes on a daily basis, the facility began its journey to turning the facility around.

It is important to note that management was understandably jaded by the regulatory process insofar as they had received incorrect information from a variety of sources as to proper management of paint wastes. The company had a plant engineer trying to "keep up" with changes in regulations on a "part-time" basis in a state known for its aggressive environmental agenda (California). Thus, he felt he had to rely on two seemingly credible sources which, in fact, caused problems. The paint salesman, whose incentive was to sell more paint, indicated that the baking of paint wastes was the "industry standard" and that it met regulatory restrictions on VOC content. (Of course, these standards have become ever more stringent in states like California or New York, so that what was an "industry standard" in one year would no longer be so a year or two later).

Perhaps more troubling was literature from its main competitor, which we presented to EPA during the negotiation phase, virtually showcasing its baking of paint waste in its ovens to reduce volume! The article was professionally produced, complete with a photograph of the proud facility operator holding a dry bucket of paint in front of a drying oven almost identical to our client's. Contributing to this problem was the fact that the competitor is a very large player in the office furniture business, and our client had to (and continues to have to) compete with far less resources, not the least of which were, and are, environmental.

After it completed the environmental and waste minimization audit, the team exhaustively researched all uses of pollution prevention settlements in administrative consent agreements. As stated above, only four cases had at the time been registered with the PPIC, which at the time was just getting underway. Additionally, we checked numerous state and Regional EPA sources for SEP-like agreements, only to be dismayed by the lack of a centrally-organized source. Not surprisingly, each Region had its own "style" or writing and disseminating such orders, resulting in difficulty in making comparisons and compiling a real profile, based on scant details of the application of the SEPs policy in many Regions' consent agreements. (The reader is cautioned that the authors believe EPA still lacks a centrally-organized, easily retrievable source of detailed SEP information. We attempted to update this paper at the time of publication only to find that although there are some gross numbers available regarding SEP settlements, see 17 Chemical Regulation Reporter 545 (BNA) 6/4/93, useful information is not easily obtainable. Neither LEXIS nor Westlaw, in addition, keep such information in particular or non-adjudicatory administrative settlements in general on line).

We were well armed when we first met with Region IX and were fluent in what we believed were the cases negotiated to that date as well as a pollution prevention plan and a number of reasons why a SEPs approach was appropriate. To our client's delight and EPA's credit, the agency recognized the effort and relied on us as a source of expert information.

We presented to EPA a very comprehensive, detailed waste management study performed at the described facility, which included raw material use, a water "budget" for all uses and processes, solid as well as hazardous waste outputs, and a comprehensive materials budgets, among other measures.

Additionally, we proposed nine <u>administrative measures</u>, aimed at correcting, influencing or empowering employee behavior. These included:

- Issuing a Pollution Prevention Policy from management to employees;
- Assigning a person or team within the plant to manage and direct the program;
- Having this person or team report progress routinely to the company president;
- Conducting employee training on pollution prevention technologies in the fabricated metal industries;
 - Monitoring of pollutant volumes more closely to observe changes and trends;
- Implementing inventory control in the paint storage room, and recycling of unused paint after six months or less;
 - Minimization of overpurchases of special colors;
 - Purchasing frequently-used colors in bulk to minimize empty containers.

We proposed nine <u>operational changes</u> fixed on hands-on solutions to direct reduction of hazardous waste/material generation. These included:

- Elimination of the unnecessary use of cardboard on the floors;
- The use of collection troughs to reduce overspray falling to the floor;
- The use of metal grating to create a better floor drainage and collection system in painting and storage areas;
- Improving paint transfer techniques in storage room using dedicated barrel pumps, funnels, spigots, or other devices;
- Installation of dedicated distribution systems for the most commonly used paint colors to minimize line flushing;
- Exploration of the possibilities of running lots of one color per week or one color per night;
- Exploration of the business pros and cons of offering a more limited choice of colors:
 - Reviewing adequacy of equipment maintenance practices;
- Reviewing adequacy of operator training and feedback for process improvement.

We made one <u>product reformulation</u> suggestion that the facility manufacture furniture of pre-coated stock (recognizing that this may be a type of "generator shift" of hazardous waste generation in that some facility would need to paint the steel).

The nine production process changes were the:

- Investigation of newer spray guns and centrifugal spray systems to reduce overspray;
- Reduction of open space between parts on the conveyor system (this greatly reduces amount of overspray);
- Consideration of painting some parts only by the Ransburg or only by the spray gun rather than by both;
- Measurement of the Ransburg's efficiency and comparison to the design specifications;
 - Reduction of the pressure in the spray guns;
 - Installation of a baffle system for the collection of overspray;
- Modification of the filter systems so as to collect less overspray (this allows more paint to go to the part);
- Review of the efficiency of the cleaning and rinsing system to reduce water use and load on the POTW.
 - Installation of a dedicated in-plant paint thinner recycling system.

Finally, we wanted to study six <u>raw material changes</u>, some of which were R&D based, in the sense that the realization of immediate benefits were less tangible, and would require some investment in time and follow-up to investigate. These changes were:

- Powder coatings;
- Water-based coatings;
- Radiation-curable coatings;
- Dip tank system innovation;

- Alternative thinners and solvents:
- Alternative cleaning and pre-coating chemicals.

As the facility implemented the Pollution Prevention Plan, we learned that certain changes worked while others did not, a situation not unexpected. For example, the total elimination of cardboard to collect overspray on the floor seemed to be a highly desirable goal because it became quite saturated and heavy and was therefore very expensive to dispose of as a hazardous waste. Several alternatives to this were explored; however, the facility returned to its use, but currently uses this procedure quite sparingly. It is not placed several layers thick, is strategically placed so as to provide maximum benefit and is removed prior to saturation. Importantly, however, its use has been curtailed by overall better housekeeping practices, advances in the use and maintenance of the spray paint systems and other behavioral changes on the part of employees, the overall result of which is continued waste minimization. This is precisely the desired effect of a rigorous pollution prevention plan in that it constantly provides the facility with feedback of its successes and failures in order to maximize beneficial alternatives.

It is important to note that the facility had, from time-to-time, investigated alternative coatings in the past; however, the company had no system or mechanism to rigorously follow new trends in the coatings industry. Again, the company was in a sense "trapped" by its small size, and was unable to participate in a program to keep it on the cutting-edge of coatings technologies which would not only help cuts its production costs but greatly benefit the environment as well.

While we discussed the SEP policies and this facility's proposed Pollution

Prevention Plan as a SEP at the December 1991 meeting with EPA, we did not think it

prudent to make the case for the Pollution Prevention Plan meriting a dollar-for-dollar

SEP setoff at that initial meeting. Our goal at that point was to get EPA interested in

how implementation of the Plan would mean long-term compliance and pollution prevention for this facility. EPA's lawyers and technical staff were cautiously enthusiastic about the possibilities of the Plan for achieving these long term compliance and source reduction goals.

At the end of the meeting, we were asked to and did prepare a detailed, written proposal integrating the Plan into the SEPs policy as applicable to this particular enforcement action, and to make clear just exactly what kind of a monetary setoff against the fine we were seeking. In preparing the written proposal, we did so because we believed in the case for such a setoff, where the proposed fine represented a substantial penalty for such a small company, where the company was sincere in eliminating the problem, and EPA staff was thoughtful and sophisticated about the issues, and seemed eager to participate in a new, developing, and promising pollution prevention program recently outlined by the Agency.

The agency responded favorably to the detailed proposal, the legal and technical personnel going out on a limb somewhat in granting what they knew would be the very first dollar-for-dollar setoff against a proposed penalty. We attached the Pollution Prevention Plan to the Consent Agreement and Final Order (CAFO) which required four quarterly reports to be made, with the consultant acting as the "third party" auditor in order to certify to EPA that the expenses and changes had been made as proposed. It is important to note that money not actually expended on implementation of the pollution prevention plan would have to be paid to EPA as an additional penalty; thus the facility owner had to fully implement the Plan as agreed. The dollar-for-dollar setoff was for the full \$218,000 for implementation of the Pollution Prevention Plan, and that after other penalty reductions, the company only paid a \$93,000 fine.

We believe EPA's policy to allow study and analysis of pollution prevention projects (unlike other SEPs) to qualify for a penalty offset is a wise one. There is

typically a series of trials and errors before the right combination of projects can be determined, and the project here was no exception to this rule.

SUCCESS OF THE STRATEGY

The attorney/consultant team's success in persuading EPA relied substantially on the fact that we helped EPA understand how full implementation of this facility's Pollution Prevention Plan would aid the agency's own goals of 1) incorporating such plans into enforcement settlements with a strong financial incentive to do so and; 2) reducing pollutant loadings to the environment, thus lowering risk to human health and the environment in the short and medium runs and; 3) improving overall environmental compliance in the long run, thus avoiding the need to expend scarce agency enforcement resources repeatedly on the same "problem" facility. We got EPA very interested at the December 1991 first enforcement negotiation meeting in having the facility implement the Plan and, more importantly, take numerous steps to ensure long-term, overall facility compliance with all environmental regulations.

Additionally, the plan was a success because

- 1. We supported the legal and policy argument that this case was ideally suited for a pollution prevention project through a highly technical evaluation of sound, implementable pollution prevention measures;
- 2. We found that sophisticated technical and legal staff at EPA understood that the facility's problems went far beyond the immediate RCRA violations that resulted from the inspection, and that therefore, the solution had to be comprehensive; we knew that ultimately these regulators were beyond a "let's hit 'em for everything they're good for" approach of maximizing the fine, and truly wanted to see the facility become compliant in an overall sense. Indeed, we found EPA staffers working on this project eager to be involved with a cutting-edge, comprehensive pollution prevention plan.

- 3. We had full support from senior company management after careful education about the benefits of pollution prevention projects, and informing them that enforcement actions could possibly recur unless attitudes genuinely changed and the level of training and professional assistance were increased; this change began with the development by the President of the company of a comprehensive policy that we did not write for him, but which we insisted that he develop based upon our discussions; based upon these developments, EPA viewed management's active "willingness...to correct a violation via a pollution prevention project" as "one of the assessment factors used to adjust the 'gravity' component of the penalty." Interim Policy at p.6.
- 4. Our plan met both the horizontal and vertical nexus requirements of the SEPs policy. It met the horizontal nexus test because decreasing the amount of hazardous wastes generated in the paint spray process would automatically reduce air pollutants generated, i.e., "relief for different media at a given facility." SEPs Policy at p.6. It met the vertical nexus test because the project would reduce the amount of paint waste created by overspray, and reduce spray paint line flushing with solvents, or entirely eliminate the use of solvents by materials substitution. Thus, this facility's SEP had a vertical nexus with the violation because the SEP "follow[ed] a violation back into the manufacturing process to address the root cause of the pollution." SEPs Policy at p. 6.
- 5. Three of the 17 targeted chemicals in the SEPs policy for reduction were used and generated as waste at the facility; these are methyl ethyl ketone, methyl isobutyl ketone, and xylene. Reduction in their use thus directly met EPA's goals to reduce the overall pollutant burden on the atmosphere;
- 6. While it was not our (or the facility's) intention to do so initially, our plan reflected a true "multi-media" approach, foreshadowing federal and state programs that were then proposed and are now underway. These initiatives represent EPA's and the states' desire to undo the historical fragmentation of environmental regulation on a

program by program basis, and to replace the patchwork system we all currently labor under with a "holistic" approach that deals with all programs and the systemic problems in management and operation that lead to environmental violations.

The company's success, on the other hand, began with the reduction in penalties assessed, of course, the relief that while an enormous amount of money would have to be expended, \$218,000 of what had been a pure penalty would at least go toward improvement of facility operations. Thus, the company's success and reward was the longer-lasting one of lower operational costs, less of the heavy, solvent and paint-saturated cardboard having to be hauled away as hazardous waste, at great expense, thus contributing to a larger bottom line. In addition, the company benefited as greater sensitization of management and employees to opportunities for greater corporate environmental citizenship took hold.

Perhaps the truly satisfying reward, however, were the results of a recent agency inspection of the facility wherein the findings reported that "all waste manifesting and profiles were accounted for" and, reflecting the long-term commitment the company made to its employees, that "training programs were in place for employees handling hazardous wastes and that training logs were signed by each employee." Additionally, all waste storage containers were properly covered, stored, labeled and were in fact detailed as "excellent." The facility is subject to California's famously rigorous SB 14 waste minimization program, and the inspection found it to be implemented "with reductions in waste production." Finally, the agency wrote:
"Significant improvements in all areas of hazardous waste management. Positive attitude of [the facility] has created an environment of reinforcing values for hazardous waste reduction and management."

LIMITATIONS OF SEPS

This paper does not discuss in detail the limitations and criticisms to SEPs, yet it would be incomplete without at least briefly listing them. Some criticisms that have been leveled are:

- 1. Pollution Prevention SEPs may provide a disincentive for voluntary pollution prevention projects.
- 2. EPA is reluctant to grant additional dollar-for-dollar settlements, and the agency has been criticized for the generosity of this particular settlement. However, the authors strongly believe that given the appropriate circumstances, potential violators should nevertheless attempt to secure a similar settlement.
- 3. The Government Accounting Office (GAO) has suggested in a July 1992 report that EPA is without authority to "divert" to corporate violators dollars that should go into the Federal Treasury. EPA intends to continue to use SEPs in settling enforcement cases until this is worked out.
- 4. Projects consistent with EPCRA and other federal and state statutes mandating pollution prevention or source reduction will not qualify for offsets because they are already required.
- 5. Once a particular company has effectively been "put on notice" by agreeing to implement a SEP, particularly a pollution prevention SEP, it will be difficult for other facilities under the same parent corporation to ignore implementation of similar programs.

CONCLUSIONS AND RECOMMENDATIONS

Pollution prevention has early on received a high profile under the Clinton Administration, and is likely to receive ever greater attention. As states turn up their environmental agendas, they will also increasingly utilize pollution prevention techniques to abate environmental penalties. Already, several successful citizen groups are using SEPs in public enforcement actions.

It is important to note the skyrocketing use of SEPs; however, equally important is the realization that these are likely used in "paperwork violations" of EPCRA and TSCA. Opportunities exist, therefore, for creative use of SEPs in more investigation-intensive enforcement actions such as RCRA violations. Should you embark on such a venture, it is our hope that you or your clients realize the overall benefits that our client gained in fully implementing a realistic and rigorous pollution prevention program.

But based on our experience in this case, and in discussing Pollution Prevention Plans with a number of clients, we believe there are certain changes that can and should be made in implementation of the SEPs program.

First, EPA must figure out a way to resolve an inherent tension between the time needed to examine and experiment with numerous possible pollution prevention projects and restrictions occasioned by certain agency requirements. These are, in particular, the apparent need to quantify project costs precisely up front in the administrative settlement, at a time when the facilty in an enforcement action wants to maximize the amount of penalty settoff, rather than defer any decision to make substantial capital expenditures pending further study of their utility to the particular facility. As the INFORM studies of 1985 and 1992 and researchers Hirschhorn and Pojasek have shown, so many pollution prevention projects do not require large capital investments so much as changes in facility attitudes and procedures. (This paper describes this very occurrence with our client). Yet EPA requires in the administrative order a fixed dollar amount of pollution prevention projects "up to which" amount an offset will be made. Thus, there is an overemphasis on both sides on selecting bigticket items (e.g., large capital expenditures for equipment replacement, which may or may not contribute to pollution prevention) in costs terms. This is an unfortunate emphasis.

The second agency requirement that is inconsistent with the trial and error nature of maximizing pollution prevention opportunities is the insistence that all

projects be completed within an artificially short time-frame, namely, in our case, only six months. It may have been a RCRA program requirement or a function of personnel caseloads and workplans, but our only disagreement with EPA after it had accepted our basic proposal was its insistence that we compress a one-year program into six months, for purposes of signing off on the Consent Agreement and Final Order. We were told informally that if things were going well, technical staff would have the discretion to extend beyond six months the time in which we had to spend the full \$218,000 that was the maximum setoff allowed in the settlement for implementation of the Plan. It is not easy to spend \$218,000 wisely in six months at a small facility when study of various alternatives, to determine the right combination of projects, itself could take six or more months. Why force facilities to spend money (failing which, the unexpended portion would be added to the penalty amount) before a thoughtful examination of what a facility needs has been completed? Pollution prevention engineering is increasingly receiving R&D investments, yet many solutions are just "out of reach" of the manufacturing sector within perhaps a dictated regulatory time frame. The SEP system should allow for such cases where a violator who genuinely wishes to participate in the "cutting-edge" of pollution prevention technology is allowed to make the proper investment over an agreed-upon time frame.

Our third conclusion and suggestion for improvement is that it is a mistake to link penalty offsets solely to the dollars expended on the pollution prevention project rather than on the amount of reduction of pollution produced by the project. Again, if the low-tech, relatively inexpensive solution results in a significant source reduction or pollution prevention, why not reward the regulated entity for its ingenuity in finding inexpensive solutions?

Our final suggestion is that the agency complete and carry out its "two percent project", between its Office of Enforcement and Compliance Monitoring, the prerequisite to finalizing the 1991 Interim Policy discussed above. Regions have in

theory been encouraged to continue to expand the use of pollution prevention conditions in enforcement settlements, as part of long-term strategic planning for multimedia enforcement, according to EPA guidances. The authors believe that this initiative must move forward expeditiously, despite the lag in EPA efforts that we are now experiencing, typical when there is a change of administrations in Washington. The concern is that as leading states like New York and California move forward with their own multi-media and pollution prevention efforts, absent a coherent and "final." not "interim" policy on such efforts, they will adopt only those pieces of EPA's program, if any at all, that seem suitable rather than the entire package. Already California, for example, has despite the leadership of California EPA Administrator Jim Strock, the author of the two 1991 U.S. EPA guidances that are the foundation of SEPs and the use of pollution prevention projects in enforcement actions, adopted a restrictive form of the SEPs program -- one in which most of the elements are in place, except that the maximum amount of setoff is only 25% of the penalty. Worse, in New York, which has begun an aggressive multi-media enforcement program, pollution prevention requirements are essential in settlements, but without any penalty setoff whatever (except for government entities for certain "environmentally beneficial" projects). Thus, there is a real potential for the States to adopt the stick without the carrot (as in New York), or without a very big carrot (as in California). We believe that restricted State budgets and the need to fund agency budgets has taken precedence over good public policy -- one that recognizes that the benefits to the society at large from pollution prevention programs are so enormous that industry deserves the maximum amount of incentive to undertake such programs.

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ARMY POLLUTION PREVENTION SUCCESS STORIES

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INTRODUCTION

The United States Army Materiel Command purchases over \$95 billion worth of equipment and supplies every year.\(^1\) To ensure that the acquisition programs purchasing these items address the life-cycle pollution prevention concept, the Army Acquisition Pollution Prevention Support Office (AAPPSO) was established in 1989. The overall AAPPSO program goal is to prevent as much pollution as possible by designing environmentally friendly equipment and support systems from the start and not simply treating whatever toxic by-products happen to be generated.

Since 1989, the AAPPSO has had a number of pollution prevention successes related to Volatile Organic Compound (VOC) and hazardous air pollutant reductions. The programs and the key success areas are listed below:

<u>Program</u>	
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Implementation of Low VOC Electrodeposited Epoxy Coating on Army equipment.

Implementation of Non-VOC based Cleaning Compounds on Army Equipment.

Replacement of Ozone Depleting Compounds (ODCs) in Army Equipment.

Success

Verified system performance. Implemented new military specification.
Started reducing VOC emissions from Army procurement activities.

Verified systems performance.
Conducted performance tests.
Implemented use of new products.

Developed technically valid substitution plan.
Started eliminating ODC based systems through redesign.

Program	Success

Elimination of Spray Chromate Conversion Coating Applications. Verified elimination process. Conducted site implementation.

The technical efforts described above will be discussed in detail. However, these successes represent only a few of the many AAPPSO project areas. Some of the other important programs being managed by the AAPPSO include; elimination of chromic acid plating rinses; development of powder coatings for Army applications, development of a technically valid, comprehensive plan for eliminating cadmium plating from Army equipment; training of Army acquisition personnel at all levels regarding the need for effective acquisition pollution prevention; development and distribution of over 6000 copies of the "Materiel Developer's Guide for Pollution Prevention;" and generation of the contractual support documents the Army requires to task contractors to implement pollution prevention.

BACKGROUND

Army industrial manufacturing processes are an essential part of the military equipment rework/overhaul process. Army manufacturing processes are quite similar to those in private industry and must comply with the same Federal, state, and local environmental regulations. Any operating or overhead costs associated with the procurement, use, or disposal of hazardous materials adversely impacts facility costs and does not contribute to an improved final product. In the past, expenses related to hazardous materials were considered a "cost of doing business." Today, through pollution prevention implementation, the Army does not have to pay for pollutants that do not add value to the product.

In addition to having to fund the normal "cost of doing business" associated with the use of hazardous materials, excessive pollutant discharges can lead to permit violations. During the 1991 - 1992, both Red River and Letterkenney Army Depots violated their air quality permits. These violations were related directly to excessive Volatile Organic Compound (VOC) emissions from painting and finishing. These permit violations have lead to significant changes in depot operating procedures.

The most effective means of saving money and preventing permit violations is pollution prevention. Pollution prevention has also been mandated as Federal and state law. The Federal Pollution Prevention Act of 1990 established an overall policy that twenty-eight states have adopted as part of their environmental regulations. Army VOC pollution prevention programs are designed to ensure compliance with these laws and to simultaneously improve product quality. Thus, pollution prevention programs help to minimize operating costs, avoid NOVs, and comply with pertinent environmental regulations.

DISCUSSION

The following discussion sections highlight the key success stories. Each discussion is roughly divided into sections describing the program background, technical results, and conclusions.

Implementation of Low VOC Electrodeposited Epoxy Coatings on Army Equipment.

In 1989, the Army Acquisition Pollution Prevention Support Office (AAPPSO), Armaments Research, Development, and Engineering Command (ARDEC), Tank and Automotive Command (TACOM), and Belvoir Research Development and Engineering Center (BRDEC) initiated a program to include the electrodeposisted epoxy (E-coat) coatings used by the automobile industry in the Army Chemical Agent Resistant Coating (CARC) family of materials. The program was designed to effectively leverage the existing knowledge within the automotive industry and thus minimize the required Army investment.

E-coat systems utilize a low Volatile Organic Compound (VOC) epoxy paint emulsion in a completely recyclable water bath. Vehicle bodies or other complex parts are electrically charged and lowered into the E-coat bath. The electric current flowing through the bath causes the epoxy paint to "plate-out" on all conductive surfaces. Because the epoxy coatings are non-conductive, current densities increase around defects or difficult to coat areas. The increased current densities cause additional coating deposition. Thus, the coating application process causes epoxy to be deposited uniformly on virtually all conductive surfaces.²

Ocean City Research Corporation (OCRC) worked with ARDEC and TACOM staff to evaluate the corrosion control performance of an environmentally acceptable, low-lead, low-VOC, E-coat formulations. OCRC prepared test panels with the proposed E-coat material and with conventional spray applied epoxy primers. Simultaneously, TACOM coated tactical vehicle bodies with the proposed materials. The panels and vehicles were then exposed to the natural marine environment for a period of one-year. Data were collected tracking the substrate corrosion allowed by the various corroding systems. Test results indicated that the proposed E-coat material provided superior substrate corrosion control performance relative to the currently applied spray epoxy primers.

Upon completion of the technical corrosion control performance evaluations, the proposed E-coat material was evaluated by BRDEC for compliance with the rigorous CARC requirements. The CARC system must resist absorption of chemical warfare agents, prevent substrate corrosion, withstand normal wear, and provide effective camouflage within the visible light and IR range. BRDEC tests indicated that the proposed E-coat material was an effective primer that satisfied all CARC performance requirements.

A new military specification, MIL-P-53084, for the electrodeposited epoxy was generated. This specification allowed Army acquisition activities to "call-out" E-coat in procurement projects. This new specification has already been invoked on the Family of Medium Tactical Vehicles (FMTV) program and will reduce VOC emissions, improve product quality, and cut costs in the near future.

The major TACOM FMTV procurement project for medium duty trucks was one of the first to require E-coat. Because the E-coat system is inherently low in VOCs and has a near 100 percent transfer efficiency, primer coating VOC emissions are minimized. Assuming that 10,000 trucks will be procured by the Army over the life of the contract, E-coat implementation could reduce primer VOC emissions by approximately 3900 tons.

In addition to VOC emission reductions, E-coat is a far more effective corrosion control primer than the older spray primer systems. Data is not yet available regarding how much corrosion control maintenance can be avoided by using E-coat. However, it has primarily been the use of cathodic E-coat over a zinc-phosphate pretreatment that has allowed the commercial automotive industry to give 7-year or 70,000 mile corrosion warranties.²

Finally, E-coat implementation will save the Army an enormous amount of money over the life-cycle of it's new vehicles. The savings will come from reduced maintenance costs, reduced coating consumption, and from being able to comply with the latest Clean Air Act Amendments. Because state air quality regulatory agencies can require Army facilities to install expensive pollution control equipment if they continue to use the older, higher VOC materials, the use of E-coat can save money through cost avoidance. At one Army depot alone, the use of E-coat could save over \$3.5 million in one time cost avoidance and over \$196,000/year in subsequent maintenance expenses.

Implementation Low VOC Cleaners at Army Depots.

Corpus Christi Army Depot (CCAD) repairs and reworks Army helicopters. CCAD had been using a wide range of VOC-based cleaning compounds in the bearing shop and airframe coating facility. AAPPSO staff worked with CCAD to identify the cleaning process parameters and develop effective measures of cleanliness for the VOC cleaning operations. Existing private industry experience was leveraged during the cleaning parameter assessment. The key cleaning parameters were then compared against the performance of currently available aqueous cleaners. Bases on this analysis, AAPPSO staff identified a non-VOC based, aqueous cleaner that could satisfy the important cleaning process parameters.

Depot staff developed a performance test program to verify aqueous cleaner system performance. Two performance test programs were initiated. The first program was designed to verify that the aqueous cleaning process could be used on high-value bearings without causing corrosion. The second program was designed to verify that the aqueous cleaner could remove soils from airframe before final coating application.

Both performance tests program were conducted at the depot using production personnel. The use of depot personnel and equipment ensured that the aqueous cleaners could not only satisfy operational requirements, but could also be implemented. Trials were conducted using the aqueous materials to clean components and airframes. The trials demonstrated that the aqueous cleaner was an effective substitute for the VOC based materials.

The aqueous cleaner based systems have been installed at the depot. Although VOC emission reductions are difficult to quantify, use of the aqueous cleaners has reduced depot operating costs. Depot personnel estimate that \$75,000 is saved every year by avoiding the costs of purchasing, handling, and treating the hazardous VOC based cleaning materials.

Replacement of Ozone Depleting Compounds

The Army uses a wide range of chlorofluorocarbons (CFCs) in fire suppression, refrigeration, and solvent cleaning systems. CFCs are considered Ozone Depleting Compounds (ODCs) because they rise to stratosphere and catalytically destroy ozone molecules. In 1988, the United States Congress ratified the Montreal Protocol which is intended to protect the ozone layer by eliminating ODC production. Broadly speaking, the Montreal Protocol increases taxes on some compounds and eliminates production of all ODCs in accordance with a fixed time-table. Because the United States, the Department of Defense, and the Army have accepted the Protocol guidelines, ODCs will have to be removed from fielded equipment and designed-out of subsequent systems.

Considering that ODCs are mentioned in over 9500 military specifications, reducing or eliminating the uses for these materials is a technically complex task.³ To manage this task, AAPPSO consulted with technical experts, industry, and the Chairman of the United Nation's "Halons Technical Options Committee." Based on these consultations, AAPPSO developed a "Strategic Plan for Replacing Ozone Depleting Chemicals in U.S. Army Tactical Weapons Systems." This plan presents solutions for the problems caused by ODCs used as fire fighting materials, refrigerants, and cleaning solvents.

The ODC plan suggests overall system replacement and existing stock conservation as the most effective means of addressing the fire fighting issues. Current Army tactical equipment typically includes hand-held fire extinguishers and an automatic fire suppression system based on the halon family of chemicals. Hand-held units are used to fight small electrical or equipment fires. Automatic units are used to extinguish fires caused by catastrophic accidents or combat damage.

The plan describes a logical process for replacing the halon filled hand-held units with similar carbon dioxide extinguishers. AAPPSO data reviews and fire analysis calculations showed that slightly larger capacity, but similar rating, hand-held carbon dioxide filled extinguishers could effectively fight the same size fires as the current Halon 1301 units. The AAPPSO intends to remove all Halon 1301 hand-held fire extinguishers from Army tactical vehicles by the end of 1995 and install the more environmentally friendly carbon dioxide based units. The Halon 1301 units will then be drained and the fire suppression chemicals collected in the ODC Reserve.

The Reserve concept is intended to ensure that the Army has enough Halon 1301 to satisfy its wartime and operational fire suppression requirements. Main battle tanks, armored personnel carriers, and most other armored vehicles have an automatic Halon 1301 fire suppression system. These systems trigger automatically when the armor is breached and

within 250 milliseconds discharge Halon 1301 to extinguish any resulting fires. What makes these systems Mission Critical is that Halon 1301 is the only material known that can extinguish the fire and not smother or poison the crew. Israeli data collected during the 1982 invasion of Lebanon showed that their halon system equipped tanks were 50% less likely to burn after being hit than non-halon equipped vehicles. Because fires destroy tanks and kill crews far more than armor penetrations alone, Halon 1301 systems are considered vital. The Army plans to stockpile Halon 1301 from hand-held units and from decommissioned systems to meet operational needs. This Halon 1301 Reserve will only be used during future conflicts. The stockpile approach minimizes the amount of halon that will have to be produced and eventually released into the environment while simultaneously providing enough material to keep these vital systems operational during combat.

The strategic plan addresses the refrigeration issue in a similar manner. Refrigeration systems are used on many modern tactical vehicles to cool electronics, food, medical supplies, and crews. Because these military cooling requirements are similar to those of the private/commercial sector, the plan suggests purchasing commercially developed non-ODC cooling systems in the future. The ODCs from current Army refrigeration systems will be collected and a one-year operational reserve kept in supply. The reserve materials will then be used on an as-needed basis to maintain and repair older ODC based cooling systems.

The strategic plan describes the use of alternative technologies to eliminate the need for ODC based solvent cleaning systems. ODC based cleaning systems are used to remove soils from delicate parts, flux residues from printed circuit boards, and as "blow-off" cleaners for precision machinery. AAPPSO determined that the ODC applications were not unique and that there are many currently available alternative cleaning technologies that could be used to replace ODCs. These cleaning technologies include aqueous washers, supercritical carbon dioxide systems, sodium bicarbonate blasting, and vacuum degreasing. The AAPPSO has communicated the need to eliminate ODC based cleaning systems to the Army acquisition managers. These managers will use AAPPSO supplied contractual documents to prohibit contractors from using ODC based cleaning systems. In addition, Army depots are conducting on-site evaluation programs for the new cleaning systems.

Considering that the ODC program is fundamentally administering the recycling of a material that will no longer be produced, the economic savings (due to the unknown nature of the future supply/demand interactions for the materials) are difficult to quantify. However, the plan is not designed to produce economic benefits, it is intended to reduce the threat to the ozone layer while simultaneously allowing the Army to satisfy vital wartime operational requirements.

Elimination of Chromate Conversion Coating Applications.

Many of the armored personnel carriers, self propelled howitzers, and transport systems used by the Army are fabricated from 5000 series aluminum. The Army has been applying chromate conversion coatings to this armor grade aluminum as a CARC system pretreatment. The chromate conversion coating uses carcinogenic hexavalent chromium to produce a pretreatment film that reportedly improves adhesion and reduces underfilm

corrosion. Red River Army Depot personnel initially thought chromate conversion coatings could be eliminated from the aluminum armored vehicles they reworked without resulting in any performance degradation. Depot staff investigated the best commercial practices and the pretreatment systems used by other services on similar grades of aluminum. This investigation revealed that commercial industry and the Navy were using more environmentally acceptable pretreatments - only the Army still required chromates on armor grade aluminum. Based on this finding, depot staff contacted AAPPSO and requested assistance with the elimination of this hazardous pretreatment.

The AAPPSO tasked OCRC to conduct a detailed technical evaluation of armor grade aluminum operational performance both with and without the chromate pretreatment. The technical evaluation was to focus on the "real-world" armored vehicle operating conditions. The test program included:

- 1. Long-term natural marine atmosphere exposure testing of CARC coated armor grade aluminum test panels.
- 2. Evaluation of both wet and dry coating adhesion.
- 3. Examination of how the alternative surface pretreatments affect resistance to Army alkaline cleaning solutions.

After completing the long-term exposure and laboratory tests, results were summarized in a final report. The report concluded that the 5000 series aluminum was so inherently corrosion resistant that the chromate conversion coating did not inhibit underfilm corrosion. In addition, laboratory testing demonstrated that primer to aluminum adhesion could be improved by using environmentally acceptable mechanical pretreatments instead of the chromate materials. Finally, the alkaline cleaner exposure tests indicated that any number of the alternative pretreatments improved overall system performance relative to the chromated test panels. These favorable results indicated that chromate conversion coatings could be eliminated from armor grade aluminum coating processes without degrading in-service performance.

The favorable technical evaluation program results led to chromate elimination trials at Red River Army Depot. Depot personnel provided a trial vehicle body and assisted with a non-chromate conversion coating implementation test. The on-site implementation test confirmed that vehicles could be coated by the depot without the chromate material. Figure 1 shows the trial vehicle coated with the standard Army three color camouflage system.

Based on technical data collected during the on-site implementation program, a specific process control document, tailored to meet the depot's operational needs, was developed. The document provides the depot staff with the process requirements and quality control tests that are needed to eliminate the chromate conversion coatings.

Elimination of chromate conversion coatings from Red River Army Depot will reduce hazardous waste generation, eliminate a worker health threat, and cut costs. Currently, chromate conversion coating rinse waters are processed by an industrial waste treatment plant, generating hazardous sludge wastes. Elimination of the chromate conversion coating will significantly reduce the waste treatment plant hexavalent chrome burden. The elimination of chromate conversion coatings from plant operations will alleviate a threat to worker health. Currently, the chromic acid based material is sprayed by a "moon-suited" worker in a booth. By eliminating this hazardous pretreatment, workers in and around the booth will not be exposed to hexavalent chromium. Finally, eliminating the chromate conversion coatings will allow the depot to avoid having to upgrade their pollution control equipment. This one Army depot alone could avoid having to spend \$4 million on new pollution control equipment and save an additional \$195,000/year in maintenance costs. Upon receipt of Command approval for the final changes, chromate conversion coatings at Red River Army Depot will be eliminated. The success of this project would then be exported to other Army production and maintenance facilities.

CONCLUSIONS

The following conclusions are based on the overall AAPPSO successes:

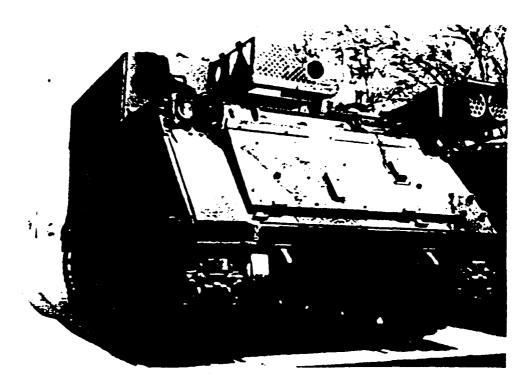
- 1. Acquisition pollution prevention programs save money. Total savings and cost avoidance from the four programs discussed in this paper for the first year are close to \$8,000,000. Additional yearly savings would exceed \$500,000.
- 2. Acquisition pollution prevention programs reduce the need for hazardous materials and protect the environment.
- 3. Management of essential hazardous materials will prevent pollution and ensure Army activities continue to have an available supply of these vital materials to satisfy mission critical needs.

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M577 Test Vehicle, Final Coating System



M577 Test Vehicle, Final Coating System

Figure 1 M577 Test Vehicle Without Chromate Conversion Coating

SESSION 5

ENCOURAGING POLLUTION PREVENTION

PAPERS PRESENTED:

"Pollution Prevention Opportunities in Coatings: Educating Those Who are Responsible for This Task"

by

Robert B. Pojasek

GEI Consultants, Inc.

Winchester, Massachusetts

"Economic Incentives to Stimulate the Development and Diffusion of Low- and No-VOC Coating Technologies"

by

Brian J. Morton

Research Triangle Institute

Center for Economics Research

Research Triangle Park, North Carolina

and

Bruce Madariaga

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina

"Pollution Prevention in the Wood Refinishing Industry"

bν

Azita Yazdani

Pollution Prevention International, Inc.

Brea, California

and

Donna Toy-Chen

City of Los Angeles

HTM Office

Los Angeles, California

"The Importance of Product Stewardship and Its Impact on Pollution Prevention"

bу

Richard S. Sayad

The Dow Chemical Company

Midland, Michigan

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

POLLUTION PREVENTION OPPORTUNITIES IN COATINGS: EDUCATING THOSE WHO ARE RESPONSIBLE FOR THIS TASK

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INTRODUCTION

Finding substitutes for regulated chemicals is an expensive proposition for the suppliers. Millions of dollars are spent in researching and development costs to make compliant chemicals available to customers. On the other side, these chemical users must spend a large amount of money to qualify the substitute chemical for its intended application. It seems that whenever a chemical gets added to yet another regulated list, vendors and users begin the quest for substitutes. Regulation creates a rather uncertain future market because it is difficult to predict which chemicals will be added to which lists. With a new administration in Washington, D.C., there are already new initiatives to expand the listing of chemicals reportable on the Toxics Release Inventory's Form R.

One way to provide some level of predictability is by the adoption of pollution prevention practices by a wide range of industrial chemical users. By increasing process efficiency, users will require lower quantities of chemicals. Perhaps they will be able to eliminate the use of certain chemicals altogether by finding new materials which do not need to be cleaned or coated. Chemical companies can then diversify into providing these new materials to industrial users.

The expeditious move to pollution prevention has started with the formation of the American Institute for Pollution Prevention. This group, initiated with funding from the U.S. Environmental Protection Agency (EPA), is an alliance of 27 trade and professional associations (see Table 1). All the information generated by EPA's pollution prevention programs is channeled into these associations to reach a broader constituency. The EPA can also tap the pollution prevention resources of these groups and their membership as new programs are initiated.

Another means of expediting the adoption of pollution prevention is by making sure that engineering students have the opportunity to learn about pollution prevention in a classroom setting. The American Institute for Pollution Prevention has sponsored an initiative at UCLA to develop a set of pollution prevention homework assignments that can be utilized in traditional chemical engineering courses. With the assistance of the American Institute of Chemical Engineers, a member association, these homework assignments were distributed free of charge to any chemical engineering professor who wanted them. In a related effort, the author has developed a pollution prevention course that can

be offered at the graduate level in an environmental engineering curriculum. A copy of the syllabus may be found in the Appendix to this article.

DESCRIPTIVE METHOD FOR POLLUTION PREVENTION

The descriptive method for pollution prevention has evolved over the four years that this course has been offered. This approach does not use worksheets, questionnaires, checklists or case histories. These are prescriptive tools. Instead process flow diagrams are used to map out the means for producing whatever product the facility is responsible for manufacturing. Process mapping allows the pollution prevention team to determine the functionality of the operation. It can be seen that one step initiates another which in turn initiates another until the process has completed its overall function with some type of product (result). Materials accounting techniques are utilized to track all materials used and lost from each unit operation. Losses include those to the air, water, solid wastes, spills/leaks, and accidents (i.e., bad batches, damaged products, fires/explosions, etc.). Activity-based costing (ABC) is utilized to allocate environmental management costs to the individual production units from the overhead which is typically spread evenly across the entire production sequence. In this manner, opportunities occurring in high ABC units will be explored first. This will help lower the cost of the operation and the pollution prevention effort will make it more efficient.

Every loss from the production units is an opportunity not to have that loss. In any manufacturing operation, there will be many opportunities for pollution prevention. In the prescriptive method, someone must look for opportunities or read about them in the available case histories or industry-specific studies. However, these approaches are not self-sustaining because the listing of opportunities is limited. Because the list is large, it must be screened with a set of criteria specific to the facility under investigation. Emphasis will be placed on the primary opportunities. Pollution prevention tools such as cause and effect diagrams, force field analysis, and dendograms are utilized to determine the root cause of the loss. Brainstorming techniques are used to derive a large number of alternatives to eliminate the loss. These alternatives are screened using effectiveness, implementability, and cost criteria derived by the pollution prevention team. If necessary, a formal feasibility study is performed on the most attractive alternatives. Some form of financial justification may be necessary to implement the selected alternative.

The Descriptive Approach is a logical, common-sense method which is nearly identical to the application of total quality management and just-in-time programs within the same manufacturing facility. Students with little knowledge of manufacturing technology can work with an industry to implement such a program after about seven weeks of the course. They finish the project at the end of the 14 week semester and it counts for 40 percent of their grade.

APPLICATION OF APPROACH TO COATINGS .

When coatings become highly regulated, the single focus of the firm using them is to find substitutes. Certainly this is the approach that the chemical companies wish to pursue themselves, since they make and sell these coatings. Some of the losses of volatile organics from the application of coatings can be improved by increasing the transfer efficiency and by other good operating practices surrounding the storage and handling of the coating medium. Efficiency translates to less coating that can be sold.

Non-VOC coatings are another option but may have other drawbacks such as poorer drying, use of flammable chemicals (i.e., alcohols), and a variety of other side effects.

The questions that the Descriptive Approach ask are: Why are you coating in the first place? Is there a material that can be used that does not need to be coated? Are there coatings with high transfer efficiencies that use no liquids? The whole idea is to eliminate the loss from a coating operation, not to substitute one loss for another. More than likely there are no ready solutions for most coating problems. However, through continuous improvement, the pollution prevention team should work towards the non-wet coating or the elimination of the need to coat by changing the base material. Many manufacturing firms end up reacting to regulations by switching to substitutes at the last minute. Sometimes these substitutes are more expensive to buy. They are always expensive to qualify.

If manufacturers practiced pollution prevention, they would be creating a predictable market for new materials and non-wet coatings. The chemical companies would diversify to capture this new market in order to cover the decreased demand for traditional coatings and low-VOC substitute coatings. Manufacturers must train their engineers to be skilled at pollution prevention techniques. Manufacturers need to see that new engineers are being trained in pollution prevention technique application. Manufacturers must see to it that the chemical suppliers are provided with an incentive to spend the money that it will take to revolutionize the way we coat materials today. This is an area where everyone can win.

TABLE 1 - AIPP MEMBER ASSOCIATIONS

Aerospace Industries Assoc. of America

Air & Waste Management Assoc.

American Petroleum Institute

American Institute of Chemical Engineers

American Academy of Environmental Engineers

American Iron & Steel Institute

American Paper Institute

American Society of Civil Engineers

American Electroplaters & Surface Finishers Society

American Institute of Architects

Chemical Manufacturers Assoc.

Electric Power Research Institute

Health Industries Manufacturers Association

Industrial Designers Society of America

National Agricultural Chemicals Association

National Association of Corrosion Engineers

National Roundtable of State Waste Reduction Programs

Solid Waste Association of North America

U.S. Department of Defense

Water Environmental Federation

APPENDIX A POLLUTION PREVENTION SYLLABUS

Department of Civil/Environmental Engineering TUFTS UNIVERSITY

CE-194J Pollution Prevention Instructor: Dr. Robert B. Pojasek Spring 1993

COURSE DESCRIPTION

This course focuses on the interface between manufacturing and the environment. By manufacturing a product more efficiently, there will be less losses to the environment. Pollution prevention examines how a manufacturing firm can move away from end-of-the-pipe pollution controls as the only means of complying with stringent regulations. A process perspective is necessary to gain an understanding of chemicals use and process losses. Information presented in the course will provide a basis for developing and implementing techniques to reduce these losses at the source.

This is a "hands on" course where the student will learn by actually working on a pollution prevention project. In lieu of a final examination, the student will work in a small group to evaluate a designated facility which manufacturers paints, adhesives, or coatings (i.e., the industry classification chosen as the focus for this semester's course). Together they will prepare process flow diagrams, materials accounting summaries, description of all of the opportunities for pollution prevention, and a rank ordering of these opportunities. Each student in the group will then research one of the primary opportunities, conduct a feasibility study, and make recommendations for implementation.

In order to learn how pollution prevention programs are planned and implemented, each student will work in another small group to evaluate a designated firm's actual program. A confidentiality agreement will be negotiated in each case before the work is commenced. Each program will be evaluated in terms of the culture of that firm and not by comparing it to other firms' programs. The group will write a report describing the program and making recommendations to improve it. Each student will prepare an individual critical review of the program.

COURSE SCHEDULE

1. January 25, 1993

INTRODUCTION TO POLLUTION PREVENTION

Without dwelling extensively on the terminology and definitional problems that currently exist in this emerging field, some generic pollution prevention concepts will be presented. These concepts will include chemical use cycles, the waste management hierarchy, sustainable development and the theories of loss control. Incentives and disincentives to the use of pollution prevention practices in industry will be examined along with pressures that have been brought to bear to induce facilities to place these practices in place. No attempt will be made to examine specific pollution prevention legislation or regulations.

2. February 1, 1993

MANUFACTURING AND MANAGEMENT

Emphasis in this course is placed on pollution prevention in manufacturing. All manufacturing categories have commonalities which, when recognized, allow the pollution prevention practioner to apply the concepts described in the previous section without regard to the type of firm. Besides examining manufacturing, the manner in which manufacturing is managed is a key to the successful implementation of pollution prevention. Analogous management programs (such as total quality management, just-in-time, and computer integrated manufacturing) will be discussed along with a model for manufacturing for competitive advantage.

3. February 8, 1993 CORPORATE POLLUTION PREVENTION PROGRAMS

One of the term papers will have the student explore how companies plan, operate, and sustain pollution prevention programs. An important key to a successful program is the recognition of the corporate culture. At various levels in the firm, this culture can vary somewhat depending on whether one looks at the corporate organization, business units/ divisions, facilities or departments in the facilities. There is also the issue of the impact of suppliers and customers in formulating a workable program to enhance competitiveness of the operation. Analogous programs such as total predictive maintenance will be examined to see how lessons learned will be applicable to pollution prevention programs.

4. Feb. 17, 1993 MAPPING A MANUFACTURING PROCESS OR OPERATION (Wednesday)

Mapping is utilized to help develop a picture of the process or operation being examined. Resolving the differences between the way different people see the process and what is actually happening is a valuable activity. A variety of mapping and other visualization techniques will be evaluated along with analogies to road maps and electrical schematic diagrams. Using process flow diagrams to help understand process functionality is at the heart of the descriptive approach to pollution prevention assessments. A variety of exercises will be utilized to develop suitable map preparation skills.

5. February 22, 1993 CONDUCTING A FACILITY ASSESSMENT

To conduct a successful pollution prevention assessment one must learn to become a good EXPLORER. Utilizing prescriptive tools (i.e., checklists, worksheets, and questionnaires) for conducting assessments have many problems associated with them. Process flow diagrams and materials accounting must be an important component of the assessment. The difference between materials accounting and materials balances will be explained. It is important that the facility assessment identify all the losses from the operations or process steps. All ancillary and intermittent operations must be identified and incorporated into the assessment.

6. March 1, 1993 IDEA TOOL BOX

Total quality management and other management programs employ a number of tools to define and understand the problems as well as to gather information for the feasibility study. Every loss identified in the assessment is an opportunity not to have the loss. To describe the opportunity and to qualify which opportunities are most important, a variety of tools can be utilized. They include: brainstorming, storyboarding, mind mapping, cause and effect diagrams, Pareto process, root cause analysis and computerized simulation models. Examples will be utilized from process equipment cleaning and chemical transfer/mixing operations.

7. March 8, 1993 ANALYZING INFORMATION

An ARTIST takes information gathered from the assessment and draws pictures with it. Graphical techniques will be utilized to present the data from the above steps. If the pollution prevention practitioner can utilize the tool box to discover trends and get at the root cause of the problems, they can begin to derive alternatives for each primary opportunity and develop the information necessary for screening and evaluation which takes place in the feasibility study. Above all, one must resist the search for the "right" answer.

8. March 15, 1993 THE FEASIBILITY STUDY

Conducting the feasibility study is like being a JUDGE. Considering the specifics in each case is important. Criteria for screening alternatives will include effectiveness, implementability and cost. A more detailed analysis of the primary alternatives will consider engineering, economics and institutional considerations. The need for bench and pilot testing must be determined at this time. All this activity will help establish a successful implementation program.

-----SPRING BREAK-----

This break provides an opportunity to work on the term papers. Four lectures will be given over the next two weeks to familiarize the student with the major categories of alternatives that are often considered in a pollution prevention feasibility study.

9. March 29, 1993 OPERATING PRACTICES/MATERIALS SUBSTITUTION

Good operating practices are often referred to as the "low hanging fruit" of pollution prevention. These are the easiest alternatives to implement and may often lead to the largest increments of reduction. Materials substitution is most frequently utilized by industry to move from listed regulated materials to unlisted materials. There are many cases where the substitute has either shifted the media into which the loss was transferred or was later deemed toxic after more detailed tests were conducted. Dematerialization is another form or materials substitution that will be covered. TERM PAPER ON COMPANY P2 PROGRAM DUE.

10. April 5, 1993 TECHNOLOGY/RECYCLE-REUSE-RECOVER

Technology can range from equipment modification and process automation to quantum leaps in the manner in which an item is manufactured. Industrial ecology is a term used to examine the concept of recycling. There is often an overlap between recycling and treatment. Each of these considerations occupy a lower status on the waste management hierarchy covered in the first class. Sham recycling and off-site operations will be examined along with the practice of waste exchange.

11. April 12, 1993 IMPLEMENTATION

Implementing the primary alternative selected in the feasibility study is often like being a good WARRIOR. Instead of fighting to get something implemented, teamwork, program integration and a good feasibility study should help facilitate project and program implementation.

12. April 19, 1993

No Class

This break will provide an opportunity to complete the pollution prevention projects which are DUE at the next class.

13. April 26, 1993

DESIGN FOR X

It is always preferable to design pollution prevention into new processes and products. The X can stand for the following terms: environment, recyclability, disassembly, remanufacturability, reliability, durability, waste minimization, etc. These terms have been in use for a long time and are all related to one another. Life cycle analysis of products is also an old tool which has taken on new meaning by including environmental impacts of operations from the extraction of the raw materials to the ultimate disposition of the final product. This analysis can utilize the descriptive approach developed in this course and need not be prescriptive. TERM PAPER ON POLLUTION PREVENTION PROJECTS DUE.

14. May 3, 1993

COURSE WRAP-UP

Each of the important lessons learned about the manufacture of paints, adhesives and coatings will be utilized to design the coatings manufacturing facility of the future.

COURSE INFORMATION

<u>Textbooks</u>. There are four texts: "A Kick in the Seat of the Pants" by Roger von Oeck (ISBN 0-06-096024-8 pbk.); "21st Century Manufacturing" by Thomas G. Gunn (ISBN 0-88730-546-6); "Facility Pollution Prevention Guide", EPA/600/R-92/088, 1992; and "Guides to Pollution Prevention-The Paint Manufacturing Industry," EPA/625/7-90/005, 1990.

Additional reading materials will be handed out each week in class along with the homework assignments.

Reserve Reading. There will be materials placed each week in the reserve reading location of the departmental library. Usually these materials will provide supplementary information.

<u>Homework</u>. Homework must be completed by the start of each class. All homework must be TYPED with adequate spacing to make written comments in the class and by the instructor. It will be discussed in the class and collected with comments written by the student as a result of the class discussion.

Grading. Each student will receive a letter grade based on the following components:

- 1. Pollution Prevention Project-Term Paper = 40% Group Report = 25% of grade Individual Report = 75% of grade
- 2. Critical Review of Corporate Program = 30% Group Report = 33% of grade Individual Report = 67% of grade
- 3. Homework: Approx. six assignments = 20%
- 4. Classroom Participation = 10%

<u>Class Schedule</u>. Each class will begin promptly at 6:30 p.m. on the dates indicated above and will end at 9 p.m.

Office Hours. Dr. Pojasek will be available one hour before every class, i.e., 5:30 to 6:30 p.m. He is also available by appointment and by telephone during the normal business day at the following location: GEI Consultants, Inc.; 1021 Main Street; Winchester, MA 01890 (617) 721-4097 (voice mail). His fax number is (617) 721-4073.

ECONOMIC INCENTIVES TO STIMULATE THE DEVELOPMENT AND DIFFUSION OF LOW- AND NO-VOC COATING TECHNOLOGIES

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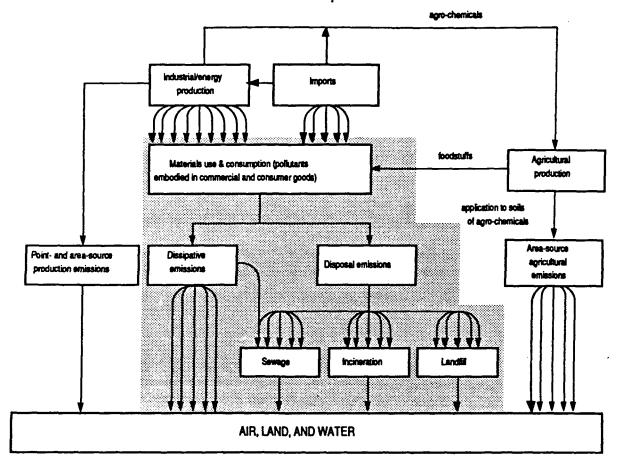
INTRODUCTION

In 1970, the year of the first Earth Day, the nation's newspapers carried a powerful image that symbolized the responsibility of everyone in a mass-consumption society for creating and solving environmental problems. This icon is the famous Pogo cartoon: "We have met the enemy and he is us."

With the exception of the regulation of automobiles, national air pollution policy has only recently addressed the environmental problems that are directly attributable to the use (as distinct from manufacture) of mass-produced consumer goods. In the Clean Air Act Amendments of 1990, the Congress directed the Environmental Protection Agency to regulate "consumer and commercial products" to reduce emissions of volatile organic compounds, which are among the precursors of ground level ozone. Section 183(e)(1)(B) of the Clean Air Act as amended (Clean Air Act) defines a consumer or commercial product as "any substance, product (including paints, consumer and commercial products, and solvents), or article (including any container or packaging) held by any person, the use, consumption, storage, destruction, or decomposition of which may result in the release of volatile organic compounds." The definition excludes fuels and fuel additives.

Thus, generally speaking, the environmental purpose of regulation of consumer and commercial products under the Clean Air Act is to reduce the flow of volatile organic compounds (VOCs) into the atmosphere from consumption (including storage) and disposal. Figure 1 shows the dissipative and disposal emissions into the air that would be the target of Federal regulation, distinguishing them from the production-related emissions that would be beyond the scope of regulation under Section 183 of the Clean Air Act (as would emissions to land and water).

Disclaimer: This paper was written by Brian J. Morton and Bruce Madariaga in private capacity. No official support or endorsement by the Environmental Protection Agency is intended or should be inferred.



Note: Shaded area indicates consumption-related emissions.

Figure 1. Comprehensive Classification of Emissions From Production and Consumption

Source: Adapted from Stigliani, William M. Chemical Emissions from the Processing and Use of Materials: the Need for an Integrated Emissions Accounting System. Ecological Economics, 2(4):325-341, 1990 (Figure 2).

Consumer and commercial products include literally thousands of specific commodities, including especially paints and other coatings. "Architectural and industrial maintenance coatings" are one subgroup of these products currently under consideration for regulation by the Environmental Protection Agency. These coatings are the source of approximately 3% of all VOC emissions in the nation. A formal negotiation is underway now to develop a Federal rule to address this important environmental problem. The rule may set a precedent for subsequent regulations involving consumer and commercial products.

Economic incentives could constitute the regulatory strategy, or one component thereof, to be promulgated under Section 183(e) of the Clean Air Act. "The regulations under this subsection may include any system or systems of regulation as the Administrator may deem appropriate, including...economic incentives (including marketable permits and auctions of emissions rights) concerning the manufacture, processing, distribution, use, consumption, or disposal of the product" [Section 183(e)(4)]. Regulations developed under Section 183(e) may be imposed only with respect to manufacturers, processors, wholesale distributors, and importers but not to retailers and users.

Economic incentives are feasible for regulating VOC emissions from architectural and industrial maintenance (AIM) coatings. Most important, economic incentives may be the most desirable type of regulatory strategy because of their potential to achieve emission reductions at lesser cost than less flexible strategies, and because of their greater potential to promote environmentally beneficial technological change.

As the nation redoubles its efforts to solve the nearly intractable problem of excessive and unhealthy levels of ground level ozone, a broad survey of the potential of economic incentives to reduce VOC emissions from AIM coatings and other coatings is especially timely. This paper surveys different types of economic incentives and compares them against the following criteria: environmental effectiveness, promotion of technological progress, economic impacts on coating manufacturers, and implementation costs.

A conclusion of this paper is that no single economic incentive will always be the best because the best program depends on policy makers' objectives. Another general conclusion is that the most helpful definition of the problem of reducing VOC emissions from coatings focuses not on reducing emissions from existing products but on providing "coating services" with fewer adverse environmental effects.

SIGNIFICANT CHARACTERISTICS OF VOCS AND OF OZONE

Volatile organic compounds and ozone have specific characteristics that influence the design of an effective economic incentive. In an airshed, VOCs mix uniformly with nitrogen oxides to form ozone, one of the main components of urban smog. The characteristic of being uniformly mixed implies that the concentration of ozone is independent of the location in an airshed of sources emitting VOCs but dependent on the total amount of VOC emissions in the airshed. Another significant characteristic of the pollutants is that at current emission rates, VOCs do not accumulate in the atmosphere from year to year, nor does ozone, and hence injury to human health and ecosystem health is due not to the historical mass of emissions but from current emissions. Therefore, cost effective incentives do not need to differentiate among the locations of sources and receptors in an airshed, and the incentives should target the rate of current emissions of VOCs.¹

BASIC MECHANICS OF ECONOMIC INCENTIVES TO REDUCE VOC EMISSIONS

The basic rationale for using economic incentives to reduce VOC emissions is to bring an environmental service provided by the troposphere—its capacity to assimilate VOCs—into the economic system.² When people release pollutants into the air, they use an environmental service without, in most cases, paying for the use of this service. While there is no cost, or an inadequate cost, to the polluter for releasing pollutants, there is a cost to all persons whose health or well-being is diminished by the resulting decline in air quality. Economic incentives for pollution control achieve their environmental purpose by increasing the cost of discarding unwanted byproducts of production or consumption to the environment.

Economic incentives directly or indirectly set the price of the environment's assimilative capacity. Fee programs may directly set the price: when the fee is charged per unit of emissions, the fee is the price. Marketable emission permit programs indirectly set the price: the price is determined by the permit market. After obtaining an initial allocation of permits from the government, permit holders buy and sell permits. These transactions determine the price of a permit. Because the permit is an entitlement to emit a certain quantity of a pollutant in a given time period, for example, one ton of SO₂ in one year, the permit price is equivalent to the price of emissions.

We know from observing ordinary markets that an increase in the price of a resource motivates users of the resource to use less. An increase in the price of gasoline, for example, motivates some people to reduce driving and others to buy more efficient automobiles. This example of the effect of a change in price and many similar examples justify the expectation that an increase in the price of using the environment to dispose of materials will lead polluters to reduce the emissions for which they are responsible.

Implicit in using the market system for pollution control is another purpose of economic incentives and another operating principle: by maintaining polluters' flexibility to respond to regulation, self-interest ensures that the amount of pollution control undertaken by a polluter is inversely proportional to the costs that the polluter incurs. Polluters will therefore be motivated to minimize the aggregate expenditure on pollution control.

Figure 2 illustrates the cost-effectiveness of emission fee and transferable emission permit programs. Two sources initially emit a total of 30 units of pollution. The government intends to reduce pollution to a total of 15 units. The government may either charge a fee of \$500 per unit of pollutant or allocate 15 permits (one unit of emissions per permit) in some way to the sources. An emission fee or a permit price of \$500 will induce Source 1 to reduce emissions from 15 units to 5 units. Source 2 reduces emissions from 15 units to 10 units. This allocation of responsibility for emission reduction minimizes compliance costs. Figure 2 shows that any other pattern of emission reductions increases total cost. For example, Source 2 would save the amount indicated by area A if it were to increase emissions by one unit, but Source 1 would spend A plus B. Theoretically, economic incentives lead to the cost-minimizing pattern of emission reductions.

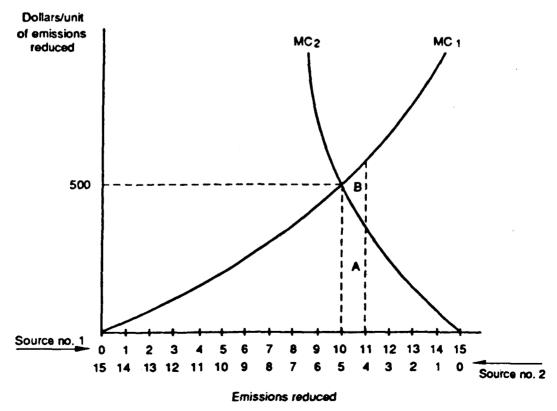


Figure 2. Cost-Effectiveness of Economic Incentives for Emission Reductions

Source: Adapted from T. H. Tietenberg, Emissions Trading: An Exercise in Reforming Pollution Policy, p. 20. Resources for the Future, Washington, D.C., 1985.

REGULATING VOC EMISSIONS VERSUS PROVIDING PRODUCT SERVICES WITH LESS ENVIRONMENTAL DEGRADATION

The purposes of any regulatory program influence the choice of specific options for the many elements in the design of a program. A primary purpose of an economic incentive to reduce VOC emissions from coatings would be to provide incentives for actions leading to the achievement of a specific reduction in total VOC emissions from the regulated products. It is important to observe that the achievement of the goal is not a one-time accomplishment but must be met on a continuous basis, therefore requiring a permanent incentive.

A significant subtlety affecting the objectives for the regulation of VOC emissions from coatings is the distinction between aiming for reduced emissions from coatings per se and aiming for reduced emissions from the means used by coating consumers to obtain the services that coatings provide. This distinction may have important implications for the design of the most environmentally effective and least expensive regulatory strategy.

The regulation of consumer and commercial products will illustrate. Regulation of consumer and commercial products under the Clean Air Act shall require "best available controls" [Section 183(e)(3)(A)]. The Administrator of the EPA, on the basis of "technological and economic feasibility, health, environmental, and energy impacts," shall determine the desired degree of emissions reduction that "is achievable through the application of the most effective equipment, measures, processes, methods, systems or techniques, including chemical reformulation, product or feedstock substitution, repackaging, and directions for use, consumption, storage, or disposal" [Section 183(e)(1)]. Best available controls refer to the emissions reduction that is determined by following the procedure specified in Section 183(e)(1).

The requirement for best available controls not only establishes the general environmental goal of regulation, it also establishes a framework for conceptualizing the thrust of regulation. Specifically, the most important feature of this framework is a focus on each individual type of consumer and commercial product: interior non-flat paint, exterior non-flat paint, clear wood preservative, and others.

A liability in the best-available-controls approach is that it encourages a tendency to overlook the environmental gains that may be available from such indirect means of emission reduction as substituting surface-coating-free materials for conventional materials. An analogy to demand-side management in the electricity market is apposite. Electricity itself is not consumed because it directly provides things that people value but because it is a source of energy for lighting and heating, which are directly consumed. The distinction between electricity and the services that electricity provides leads to a recognition that society may be better served not by imposing high-cost emission control requirements on coal-burning power plants, but by reducing electricity demand through, for example, policies that increase the efficiency of using electricity. For similar reasons, the design of regulations to reduce VOC emissions from coatings should not overlook options for promoting substitute no-VOC technologies.

Obviously, this argument in favor of pollution prevention is a familiar one. Yet the combination of pollution prevention and economic incentives is a rather unexplored part of the policy terrain. A survey of economic incentives to reduce VOC emissions and to promote low-and no-VOC coating technologies will illustrate the pollution prevention opportunities that may be seized with the use of economic incentives.

SURVEY AND COMPARISON OF ECONOMIC INCENTIVES TO REDUCE EMISSIONS AND TO PROMOTE LOWER-VOC COATING TECHNOLOGIES

Economic incentive strategies designed to achieve emission reductions typically work by directly imposing a cost on the polluter, or the manufacturer of a polluting product, for the emissions for which he or she is responsible. Policy-makers have many strategies from which to choose. Further, the choice is complex because multiple criteria are relevant to the choice of regulatory strategies. The following criteria, although not exhaustive, are among the most important for economic incentives to reduce VOC emissions from coatings:

- · certainty of air emissions reduction,
- probable implementation cost,
- potential for adverse economic impacts on coating manufacturers, and
- potential to promote technological progress.

To facilitate the comparison of regulatory strategies, we use a system of qualitative rankings that indicates relative performance on a criterion. Therefore, for example, the specific meaning of a ranking of poor on a criterion may not be indicated precisely, but the difference in performance between poor and fair is less than the difference between poor and excellent.

A full comparison of regulatory strategies should account for both direct and indirect effects. Any strategy that serves to increase the cost of employing VOC-containing coatings will simultaneously stimulate development of lower-VOC technologies such as coating-free surfaces. For example, coating-free surfaces are substitutes for surfaces that require coating. If the cost of coatings is increased, the relative cost of coating-free surfaces will decrease, and demand and prices for coating-free surfaces will increase. Higher selling prices for coating-free surfaces will then stimulate technological developments. Consequently, over time, the indirect effects of VOC regulation include an increased demand for substitute products and an increased supply of new substitute products.

The rate of technological innovation is sensitive to the regulatory strategy. Though command-and-control strategies that increase the cost of producing or consuming high-VOC coatings will encourage development of low-VOC technologies, economic incentives may be used to stimulate technological development in a more effective and sustained manner.³

An economic incentive, such as VOC content fees or VOC allowance trading, provides a continuous incentive for polluters to reduce emissions. Command-and-control strategies, for example, VOC content limits and mandated technological requirements, provide a one-time increase in the cost of using high-VOC coatings. After compliance, polluters do not have a continuing incentive to reduce emissions further. However, polluters who must pay an emission fee have a continuous incentive to develop technologies to reduce emissions and hence to reduce fee payments. Similarly, when participating in an emission trading program, polluters have a continuous incentive to develop emission-reducing technologies in order to sell more or buy fewer allowances.

Various fee-based strategies can be employed to increase the private cost of producing or consuming VOC-containing coatings. Examples of such strategies include:

- (1) simple emission fee—constant or variable fee rate per unit of VOC,
- (2) emission fee with rebates—fee revenues are rebated to manufacturers,
- (3) emission fee over VOC threshold—fee is levied only on emissions from products of which the VOC content exceeds a threshold, and
- (4) VOC reduction subsidy—fee paid by government for each unit reduced.

Table 1 summarizes our evaluation of each of the regulatory strategies discussed in this paper.

In the group of strategies labeled as a "simple emission fee," a fee is levied on all emissions, and, at any point in time, each source faces the same fee rate. A constant fee provides a diminishing incentive for emission reduction and technological progress if inflation occurs. Further, as the economy grows and the volume of coating sales increases, emissions will also increase.

Variable rate fees are essential to forestalling an eventual increase in aggregate emissions from the regulated products, and even so the level of emissions will be uncertain. A prespecified formula can be used to link the fee rate to the level of emissions reduction progress from some baseline. Although advance notice of the conditions under which the fee will change does enhance the formation of expectations, one potentially serious disadvantage of this strategy is planning uncertainty for sources because emissions reduction progress is uncertain and hence the fee rate will change unpredictably. Planning uncertainty increases the adverse economic impact on coating manufacturers.

The potential of a simple emission fee to promote technological progress is very good, but the potential for adverse economic impacts on coating manufacturers is high. The certainty of emissions reduction is fair even with a variable rate fee because of the difficulty of predicting the short-term responses to a fee, although repeated adjustment of the fee rate will close the gap between expected and actual reductions. The probable implementation cost is moderate, reflecting the regulator's need for: product-by-product information on coating sales, VOC content of each regulated product, laboratory testing of sampled products, and each regulated source's remittance.

Fee strategies with full or partial rebates are attractive because rebates can reduce economic impacts on manufacturers. By rebating fee revenues based on market share or any other criterion unrelated to emissions, incentives to reduce emissions and to develop lower-VOC technologies can be maintained. Incentives for technological diffusion, however, may be reduced if revenues are rebated. A manufacturer that develops a new technology will be more reluctant to sell an innovation to other manufacturers, because to do so would reduce the latters' fee payments, resulting in reduced rebates to the manufacturer selling the technology. Because a manufacturer also could lose its competitive advantage by selling its technology to competitors, the total incentive for technological diffusion is especially low in a fee program with rebates. The total incentive for technological change is less in comparison to fee strategies without rebates. The record-keeping associated with rebates increases the regulator's implementation costs.

TABLE 1. RANKING OF REGULATORY STRATEGIES TO REDUCE VOC EMISSIONS FROM SURFACE COATINGS

RELATIVE RANKING							
Strategy	Potential to Promote Technological Progress	Potential for Adverse Economic Impacts on Coating Manufacturers	Probable Implementation Cost	Certainty of Air Emissions Reduction			
Simple Emission Fee	Very Good	High	Moderate	Fair			
Emission Fee With Rebates	Good	Low	Moderate to High	Fair			
Emission Fee Over VOC Threshold	Limited	Low to Moderate	Low to Moderate	Fair			
Emission Reduction Subsidy	Very Good	None	Moderate	None			
				1916 C. 3 S. J. L.			
Allowances	Fair	Low to Moderate	Moderate	Excellent			
Marketable Allowances	Very Good	Low	Moderate to High	Excellent			
Auctioned Allowances	Excellent	High	High	Excellent			
Cross-Line Averaging	Fair	Low to Moderate	Moderate	Poor			
Substitute Product Subsidies	Good	Low	Moderate	Fair			
Substitute Product Research Grants	Very Good	Low	Low	Poor			
Combination Fee or Auction with Substitute Product Subsidies	Best	Highest	Moderate to High	Good or Excellent			
Command and Control (Content Limits or Technological Requirements)	Poor	Moderate to High	Low	Good			

Another strategy to reduce the adverse economic impact on manufacturers from fees combines an emission fee with a VOC content threshold. A fee would be levied only on emissions from products of which the VOC content exceeds a specified threshold. Depending on the threshold, this hybrid strategy is likely to reduce fee payments in comparison to a simple fee strategy. It may also may reduce administrative costs because only sales and VOC content of coatings exceeding the VOC threshold need to be monitored. A drawback with this strategy is that incentives for technological innovation are limited because no incentive would exist for reducing VOC content below the threshold.

Another pricing strategy that can be employed to reduce emissions from coatings is a per unit emission reduction subsidy or negative fee. Instead of manufacturers paying a fee for each unit of VOC emitted, the regulator would pay manufacturers a subsidy for each unit of VOC reduced below some baseline. This strategy unambiguously benefits manufacturers while preserving their incentive to reduce emissions. The subsidy would create an opportunity cost of using VOCs: forgone subsidy receipts. Provided that the rates are equal, an emission reduction subsidy and an emission fee have the same potential to promote technological progress.

Unfortunately, there are at least two major problems associated with the subsidy approach. The most obvious problem is one of funding such a program. A less obvious problem concerns the long run "entry/exit" impacts associated with subsidizing emission reductions. Subsidies make the subsidized industry more profitable, thus discouraging exit from the industry and encouraging entry into the industry. Though each manufacturer has an incentive to reduce emissions, the number of manufacturers could increase. It is entirely possible that aggregate emissions could increase in the long run (after entry) with an emission reduction subsidy.

Various emission trading strategies can also be employed to increase the private cost of producing or consuming VOC-containing coatings. Examples of such strategies include:

- (5) simple allowances—VOC allowances for each source,
- (6) marketable allowances—trading among sources is permitted,
- (7) auctioned allowances—the initial allocation of allowances is made via auction, and
- (8) cross-line averaging—sales weighted average limits.

As with fee strategies, different emission trading strategies perform differently on the evaluation criteria. For the group, the cost of implementation is unlikely to be low because the regulator must keep track of allowance holdings as well as monitor emissions. With the exception of cross-line averaging, the trading strategies in this list cap aggregate emissions from the regulated sources. The first three trading strategies offer unmatched certainty of air emissions reduction; conversely, as explained below, cross-line averaging performs poorly on this criterion.

The simplest trading strategy works by distributing VOC allowances to each source based on historical emissions, product market share, or some other criterion. Sources choose their own least cost strategy to reduce VOCs under their "bubble." If the emission constraint implied by the distribution of allowances is binding, each source will have a fair incentive to develop or adopt lower-VOC technologies. Lower-VOC technologies generate an internal supply of excess allowances that may be consumed by new coatings or increased sales of reformulated coatings. A source's gain from excess allowances is limited because he or she may not sell allowances to another company. The prohibition on interfirm trading severely limits the incentive for technological progress.

Any particular source's incentive for technological innovation and aggregate (industry wide) control cost savings will be augmented, however, if sources are allowed to exchange (buy or sell) allowances with other sources. Interfirm trading increases flexibility for responding to the increased private cost of emissions. A source may find that external sources of emission reductions are cheaper than internal sources. The prospect of selling excess allowances (or buying fewer allowances) provides a stronger, continuing motivation to invent lower-VOC technologies. The incentive for technological progress is very good, but not as high as possible because, as we explain next, the greatest benefit to an innovator occurs when allowances are auctioned.

The regulator may sell allowances at an auction instead of giving them away. Theoretically, at an auction, sources immediately obtain the quantity of allowances that allows them to achieve the cost-minimizing configuration of emission reductions, given current conditions. Allowances are thus distributed predominantly to sources whose control costs are high. Auctions avoid the time and transaction costs associated with trading, and they immediately establish an obvious market price, which facilitates the evaluation of future investments in emission reduction.

An auction allowance strategy could also increase the rate of technological progress. Although the incentive for each individual manufacturer to develop new technologies does not depend on the method used to distribute allowances, the distribution method does affect the private gains from diffusion. Under an auctioned allowance strategy, all participants would gain from the diffusion of low-VOC technologies in order to drive allowance prices down. This gain from diffusion is absent from allowance strategies in which the regulator gives allowances to sources. Therefore, the potential of an auction allowance strategy to promote technological progress is excellent.

A potential problem with an allowance auction is a substantial adverse economic impact on sources because they must purchase allowances from the regulator. It is possible to devise revenue-neutral auctions that minimize these impacts.⁴ In a revenue neutral auction, all payments for allowances are kept within the industry; in effect, the regulator rebates payments for allowances. However, these rebates lessen incentives for technological diffusion.

In the context of this paper, cross-line averaging is another emissions trading strategy in which trades may only occur within a facility or company. A single sales-weighted average VOC content limit is imposed on each source. Thus each source's total rate of VOC usage or production is limited. Unlike the emission trading strategies discussed above, cross-line averaging does not cap aggregate emissions. Each source is given flexibility to use or produce high-VOC coatings if it compensates with sufficient use or production of low-VOC coatings. If a source's actual weighted average is binding, the source will have an incentive to develop low-VOC coatings or employ low-VOC technologies so that high-VOC coatings or technologies can also be used. Because of the similarity of cross-line averaging and allowances without interfirm trading, the potential of averaging strategies to promote technological progress is only fair.

A potentially serious problem with cross-line averaging strategies is that sources may act opportunistically, defeating the environmental objective of the strategy. For example, sources may sell inexpensive low-VOC coatings at reduced prices to reduce their sales-weighted average VOC content. If this were to occur, aggregate emissions could increase. The certainty of emissions reduction with this strategy is very low.

All of the above emission fee and emission trading strategies work by increasing the cost of producing or consuming VOC-containing coatings. Another approach to motivating VOC reductions is to directly decrease the cost of developing or producing no- or low-VOC substitutes for coatings. Two such strategies are:

- (9) substitute product subsidies and
- (10) research grants.

For example, subsidies could be employed to promote the development or sale of substitutes such as coating-free surfaces. Ideally, the level of substitute product subsidies should be directly related to expected VOC reductions. Indirect product subsidies are also possible through tax credits. Lump-sum subsidies such as research grants may be easier to administer, though they provide less certainty regarding emission reductions. Grants could directly promote technological innovation and may also encourage technological diffusion if they are made contingent upon early public disclosure of new developments.

Unlike per unit VOC reduction subsidies, subsidies to promote the development or sale of coating substitutes (or no-VOC as opposed to low-VOC coatings) avoid entry-exit problems that could result in long-run emission increases. Increased profitability and entry could not result in increased emissions if the substitute product emitted zero VOCs. However, the problem of funding such subsidy and grant strategies would still exist.

Substitute product subsidies and research grants have a good to very good potential to promote technological progress, but the certainty of emissions reduction is very low because any improvement occurs solely as a result of technological innovation and diffusion. Any adverse impact on coating manufacturers will occur as a result of the diffusion of products that reduce the demand for coatings. Implementation costs are likely to be low to moderate; linking subsidies to expected VOC reductions is likely to require somewhat extensive economic and engineering modeling.

One way to fund substitute product subsidies and research grants is to obtain revenues from an emission fee or an auctioned allowance strategy [(1), (3), and (7)]. Therefore, a combination strategy may be desirable:

(11) combination emission fee or permit auction with no-VOC product subsidies

Such a combination VOC reduction strategy would provide the maximum incentive to develop lower-VOC technologies. It may also encourage coating manufacturers to jointly develop and share low-VOC technologies because technological diffusion would result in lower subsidy payments to no-VOC competitors such as producers of surface-coating free materials. Depending on whether the incentive is an emission fee or a marketable emission permit, the certainty of emissions reduction is good or excellent, respectively. The disadvantages of these strategies are an especially great likelihood of adverse economic impacts on coating manufacturers and high implementation costs.

Authority for States to implement a combination strategy such as (11) is granted by the Clean Air Act Amendments of 1990. Section 182(g)(4)(B) explicitly states that revenues generated by an economic incentive program may be used to provide incentives to achieve additional emission reductions and, more specifically, may be used to encourage the development of lower-polluting solvents and surface coatings.

The last strategy that we evaluate is a command-and-control strategy:

(12) VOC content limit or technological requirement

Almost all the rewards that innovation and diffusion bring to sources under the other strategies are absent. Because these gains are minimal, a command-and-control strategy performs especially poorly in terms of the potential to promote technological progress. Another disadvantage is the moderate to high economic impact on coating manufacturers; the impact is potentially substantial because sources do not have flexibility to find the least costly means of reducing emissions. Implementation costs are probably low because the regulator does not absolutely need to keep track of emissions for purposes of determining compliance. The emission reductions that this type of strategy can achieve are certain in the near term, but they will be eroded in a growing economy.

Table 1 illustrates the numerous tradeoffs that need to be considered when selecting a regulatory strategy to reduce VOC emissions from surface coatings. The rankings are based on an "all else equal" principle and will obviously not apply in all cases. Other criteria that are important, such as consumer and taxpayer impacts and political feasibility, were not assessed for reasons of brevity.

CONCLUSIONS

Overall, economic incentives provide substantial advantages over command-and-control strategies to reduce VOC emissions from surface coatings. In general, economic incentives are superior with respect to minimizing aggregate expenditure on pollution control (i.e., cost-effectiveness) and promoting technological progress. The potential for adverse economic impacts on coating manufacturers tends to be lower with economic incentives. Allowance-based economic incentives are unique for their ability to cap emissions.

Nevertheless, command-and-control strategies may still be preferable if monitoring, record-keeping, and other implementation activities are significantly less expensive than with economic incentives. Hence the choice between strategies depends greatly on the size of the additional implementation costs associated with economic incentives.

The "optimal" economic incentive strategy depends on the policy-makers' objectives. If stimulating technological progress is considered of most importance, a combination incentive strategy such as (11) may work best, but this strategy could impose severe impacts on coating manufacturers. All of the economic incentive strategies examined in this paper lead to more rapid technological progress than would result from command-and-control strategies, but some provide more stimulus than others. All of the economic incentive strategies lead to more cost-effective emission controls than would result from command-and-control strategies, but some imply fees, allowance prices, or subsidies to competitors that could severely affect coating manufacturers. If certainty over reducing air emissions is of most importance, then emission trading strategies are best. It is therefore essential that policy-makers determine objectives and priorities before selecting a regulatory strategy.

Finally, in keeping with the pollution prevention approach, a full appraisal of the desirability of economic incentives includes an examination of the potential for unintended damages. The hypothetical programs examined in this paper have been narrowly focused on VOC emissions, but the environmental problems in manufacturing and using coatings are interdependent. Narrowly defined solutions may be counterproductive when imposed on complex problems. Intermedia transfers of pollutants could occur if reformulated products are more prone to off-specification manufacture or have a shorter shelf life. Manufacturers may reduce VOC content by substituting a noxious solvent or propellant, which could increase health risks to workers and product users. A coating with reduced VOC content may produce a less durable film than a higher-VOC formulation, potentially leading to increased emissions over the life of the substrate. VOC content limits appear to be more prone to these problems than economic incentives because limits are more likely to constrain manufacturers' product design options. This may be another reason to prefer economic incentives over less flexible strategies.

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Pollution Prevention in the Wood Refinishing Industry

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Introduction

Pollution Prevention International, Inc. (PPI) under contract to the City of Los Angeles conducted a pollution prevention study of the wood refinishing industry. PPI reviewed the common coatings processes and hazardous material management practices utilized by this industry. PPI evaluated alternative water-based and low VOC coatings utilized at various facilities. In addition, PPI conducted a workshop for the City of Los Angeles refinishing industry users to share the information about the alternative technologies and new coatings systems application.

Industry Overview

The wood refinishing industry in Los Angeles consists of furniture and cabinet refinishing, reupholster and repair shops. These shops are engaged in the repair and refinishing of household and office furniture and fixtures (both metal and wood), kitchen cabinets and particle boards. Approximately 300 shops in this industry sector are licensed within the City. The majority of these shops are small companies with three to seven employees. In the City of Los Angeles, only one shop employed about 60 employees and three shops employed about 15 employees.

The industry is primarily focused in Los Angeles' furniture district, with most shops engaged in refinishing and restoration of antiques. About ten percent of the companies were contacted by PPI to set up site visits and review operation and practices.

The basic refinishing steps that most of these shops followed are as following:

- 1. Remove old finish, using chemical stripping or sanding
- 2. Sand, stain, (and bleach) the surface
- 3. Fill the pores

4. Apply sealer

5. Add transparent or colored film coat

A number of different chemicals are used in any of the above processes. These may include:

Cleaning: petroleum distillates, alcohol Stripping: methylene chloride, acetone

Staining: mineral spirits, alcohol, pigments Painting: toluene, glycol ethers, pigments

Finishing: resins, shellacs, toluene, diisocyanates

Equipment Cleaning: petroleum distillates, 1,1,1-trichloroethylene,

alcohols

Regulatory Requirements

There are a number of regulatory requirements that impact this industry sector. These are primarily hazardous waste and air quality requirements.

The South Coast Air Quality Management District (SCAQMD) is responsible for controlling air pollution and attaining federal and state air quality standards in Southern California. The regulations limit the content of Volatile Organic Content (VOC) of the coating or the solvents used by these shops. All refinishers are required to have a permit, whether or not they operate a paint booth. The annual emissions must also be reported by each facility.

The SCAQMD Rule 1136 and 1171 are the two major rules that impact refinishing operations. Rule 1136 limits a facility on the use of high VOC coatings that are used on wood products. A coating can not be applied which exceeds the limits in Table 1. The amount of coating used at the facility must be recorded to demonstrate the quantity of emissions from the facility.

Proper application equipment is required when applying coatings. SCAQMD allows for the following applications equipment:

- electrostatic
- flow coat
- dip coat
- high volume, low pressure (HVLP) spray
- paint brush
- hand roller

Rule 1171 regulates solvent cleaning of application equipment. The rule states that a cleaning solvent shall not have a VOC content greater than 950 grams per liter of material and a VOC composite partial pressure of 35 mm Hg or less at 20C (68F). Common VOCs found in cleaners are methyl ethyl ketone and acetone. Cleaning processes allowed by Rule 1171 includes systems that totally enclose cleaning equipment used to flush the part in a controlled manner. Wipe cleaning and spray cleaning with a maximum container of 16 fluid ounces are also allowed.

The refinishers have to also comply with the various regulatory requirements applicable to hazardous waste generators. These requirements are not discussed in this paper. It should be noted that in California there is no exemption for small quantity generators, thus these facilities have to comply with the regulations without regard to all the waste generated, such as clean-up solvents, contaminated rags and waste paint.

Summary of Site Tours

Six facilities were toured during this study to explore the management practices and assess regulatory compliance status of each plant. Of these, four plants were actual refinishing plants. The other two were furniture manufacturers.

Three of the refinishing plants visited were very small facilities. The users at these facilities were for the most part not in compliance with the various regulatory requirements in place. One plant utilized a spray booth without a permit. This plant, an antique furniture refinisher, was not willing to disclose many of the management practices it utilized. For example, the plant generated no hazardous wastes although it engaged in stripping and coating of various wood, iron, and cement parts. Isopropyl alcohol or methylene chloride were used for stripping purposes. For the most part, the chemical was applied on the part, then the coating was scraped off after some time. The rags utilized by the workers were soaked in water after use. This water is then illegally disposed down the sewer. The rags were either reused or disposed in trash. This refinisher had started experimenting with some water based lacquers. He sealed the part with solvent based material and then sprayed water based top coatings. This plant also did not utilize the required application equipment, such as HVLP guns.

The next refinisher engaged in refinishing and refurbishing of old pieces. He has switched to water based coating, primarily because of the look and texture that the water based materials gave his work. This facility did not restore pieces that require the high polished lacquer look, therefore there was no need to utilize these types of coatings. No chemical stripper was used at this facility, only mechanical (hand) sanding was done. This user

had never managed any of his leftover chemicals or rags as hazardous waste. He used water to clean application equipment. The water was kept in a bucket then dumped on the floor to dry out. This refinisher complained about the SCAQMD requirements and how he did not have time to keep track of the paint usage records and prepare the reports required.

The other small refinisher visited used both water based and acrylic material. The facility had a permitted spray booth and he used conventional guns to coat. He coated a mixture of old and new pieces, thus a variety of coating materials are used at this shop. He did not manage any waste as hazardous waste although he generated some thinner from gun cleaning and other cleanup operations.

The last refinisher visited was a large job shop that engages in refinishing, painting, and upholstery of office and commercial clients. This facility employs as many as 75 personnel at times, and complies with the regulations from both air quality and hazardous wastes. This facility had experimented with water based material but found that the water based lacquer chips, causing problems for the customers. Also parts coated with this material can not be touched-up. The facility had two permitted spray paint booths which utilized HVLP guns, and used gun cleaning stations to clean application equipment. Lacquer thinner was primarily used for this purpose, which is sent for disposal at a cement kiln for resources recovery. The filters in the booths is also disposed as hazardous wastes. The facility spent as much as \$15,000.00 annually to dispose of hazardous wastes. This facility also used stripping chemicals which was hauled as hazardous waste when used and wash thinner (TCA-based) was used to clean equipment or dilute coatings. This material was reused until no longer useful.

Two finishers were also visited, one small and one large. The large facility mass produces furniture using 50 tons of coatings per year. The furniture was put together, sanded, and finished on an assembly line process. The fastening and sanding was done by hand power tools. The finishing was completed on the assembly line, in the open air, with air assisted airless spray guns. Two applications of clear coat solvent-based lacquer were applied in most cases, within ten minutes of each other. In one hour, the piece of furniture was boxed and ready to go.

The second finisher visited produces high quality, custom furniture. It designs and formulates its own coatings. All of the furniture is also fabricated at the shop. The furniture is put together, sanded, and then finished. The finish is applied by HVLP spray guns in a spray booth. The finish is one thick coat application of an opaque solvent based coating. The coated piece is then cured for several hours in a "clean room". The results

are high quality flawless rock hard coatings. This facility uses less than 4 tons of coatings per year.

Study Findings

The majority of the facilities visited were small quantity hazardous materials users and waste generators and were in violation of basic regulatory requirements for air quality, hazardous waste, and hazardous materials management.

Most users were not familiar with the regulatory requirements governing their industry, and did not have the necessary permits to operate their business. PPI also found that most of the facilities had problems with record keeping and calculations that needed to be conducted on a daily basis to comply with the SCAQMD rules and regulations.

The impact of air quality regulations on the industry is most significant. The SCAQMD rules are primarily written for larger furniture manufacturing and coating facilities and the regulatory requirements for smaller users is cumbersome.

All refinishers except the largest refinishing facility did not meet hazardous waste management requirements, including hazardous waste disposal, manifesting, and generator requirements.

Pollution Prevention Techniques and Technologies

As mentioned earlier, the majority of the users participated during the study had major problems with the application and implementation of the regulatory requirements. However, the various pollution prevention techniques were reviewed and discussed during facility visits, so users will become familiar with the requirements. The following is a summary of the various pollution prevention opportunities that were identified for this industry sector.

EQUIPMENT MODIFICATIONS

There are a number of new equipment technologies that can be utilized by the paint and coating users to reduce paint usage and overspray. One type of technology that has become widely utilized in recent years is the High Volume Low Pressure paint gun systems. These systems allow the use of low pressure airstream at high pressure to propel coating at the transfer efficiency of 65-95 percent. This type of technology has been widely used in the wood industry in the recent years.

ALTERNATIVE COATINGS

There are a number of alternative materials and processes that are used throughout the wood industry. These coatings are reviewed below:

Waterborne Coatings - Waterborne coatings are used in some sectors of the wood industry with documented success. This type of coating contains low VOC so is favored by the air regulatory agencies. The slower drying time is sometimes a concern for users with high volume production. The water borne material may also raise some wood surfaces, requiring extra sanding and preparation steps. Some VOC solvents are normally used in these formulations, however, the low VOC concentrations is still an advantage over conventional coatings. Commonly, electrostatic application equipment is recommended for high volume spray application.

High Solids Coatings - These coatings contain as much as 30 percent solvent and up to 55 percent solids by volume. Although these coatings are low in VOC, they have high viscosity and applications with spray equipment is more difficult. The high solids content of these coatings require high drying time, resulting in shorter pot life. The application equipment must be routinely maintained. Paint "Orange" peeling and solvent popping are also some of the problems of these coatings. The use of these types of coatings in wood industry is limited.

UV and IR Curable Coatings - These coatings are used in less than 5 percent of the wood refinishing market due to the cost of the equipment and limitations for uses such as refinishing. The transfer efficiency of these coatings is 95 to 98 percent, and they contain no solvent. The conventional spray equipment can not be used for the application of this technology.

Study Conclusions

PPI and the City of Los Angeles concluded that small facilities engaged in this industry sector have to comply with regulations that are too complex and time-consuming for a small facility. The industry will respond to a regulatory assistance program that does not prevent these small businesses from running their day-to-day operations and will assist them in complying with the maze of regulations. The City of Los Angeles has considered making the following recommendations to the SCAQMD to assist the refinishing industry to comply with the requirements:

 Exempt this industry sector from all record keeping and reporting requirements for air quality regulations;

- Increase transfer of information between industry and developers of technologies; and
- Mobilize industry to interface with regulatory agencies and regulators.

TABLE 1
Current VOC Emissions Limit
Rule1136 (August 1991)

		V	OC LIMITS							
		Grams Po								
		Less Water and Less Exempt Compounds								
			•	D AFTER	ON AND AFTER					
			7/1	/94	7/196					
COATING	(g/L)	(lb/gal)	$\overline{(g'L)}$	(lb/gal)	(g/L)	(lb'gal)				
Clear topcoats	550	(4.6)	275	(2.3)	275	(2.3)				
Filler	500	(4.2)	500	(4.2)	275	(2.3)				
High-Solid Stains										
Non-glaze	700	(5.8)	700	(5.8)	240	(2.0)				
Glaze	700	(5.8)	700	(5.8)	240	(2.0)				
Inks	500	(4.2)	500	(4.2)	500	(4.2)				
Mold-Seal Coating	750	(6.3)	750	(6.3)	750	(6.3)				
Multi-Colored Coating	685	(5.7)	275	(2.3)	275	(2.3)				
Pigmented Coating	600	(5.0)	275	(2.3)	275	(2.3)				
Sealer	550	(4.6)	550	(4.6)	240	(2.0)				
Strippers	350	(2.9)	350	(2.9)	350	(2.9)				
Low-Solids Stains										
Toner, or Washcoat	480	(4.0)	480	(4.0)	120	(1.0)				

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The Importance of Product Stewardship and Its Impact on Pollution Prevention

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Product Stewardship can be an important factor in helping businesses maintain that their products are being used safely by workers who handle the products, from the time they are shipped to the time they are disposed. Committing the time and effort now to a Product Stewardship Program is an essential investment in the future of our industry.

Experience suggests that many organizations haven't had the opportunity to completely explore the positive impact Product Stewardship — throughout the whole life cycle of the product — could have on its business as well as its customers. And they haven't had the opportunity to develop programs with and for customers. The following information will help explain Product Stewardship throughout the life cycle of the product, how it works, the responsibilities involved and the benefits.

THE MEANING OF PRODUCT STEWARDSHIP

Product Stewardship is more than just a program. Most programs have a beginning and an end. Rather, Product Stewardship is an ongoing process — a continuous activity that is used to: (1) obtain the proper health, environmental and safety data for our products; (2) evaluate uses and (3) take appropriate steps to protect human health, safety and the environment. This last statement especially, take appropriate steps to protect human health, safety and the environment, is the correlation between Product Stewardship and pollution prevention. Pollution is one of the causes leading to an unhealthy environment and environmental concern. Preventing pollution is an element of Product Stewardship — a way to take action to keep the earth safe and healthy for future generations.

Basically, Product Stewardship is an investment of resources, time, and capabilities. It's knowing the full capability of our products and explaining those capabilities to the users. It's conducting the various safety tests and providing notification through material safety data sheets and proper labeling. Product Stewardship is more than a commitment to develop data for the safety of our products and our customers. It's a commitment to help customers understand our products and how to use them. To work with them so they can help themselves.

THE RESPONSIBILITY AND COMMITMENT TO PRODUCT STEWARDSHIP

You may be thinking to yourself right now, "I wish it were just a program, never-ending sounds awfully time consuming — and expensive." Well, you may be right in one respect — it is a major commitment. Should you choose to embark on the path to Product Stewardship, it will become a continuous process. But over time, you are likely to stop thinking of it as a "never-ending program" and begin seeing it as a better way of doing business.

Who Is Responsible?

The responsibility of Product Stewardship is covered throughout the whole product life-cycle as explained in the "Codes of Management Practices and Product Life Cycle" chart. This chart is part of a program called Responsible Care. — the CMA (Chemical Manufacturers Association) initiative developed to respond to the questions and concerns of the public surrounding our industry. The aim of Responsible Care is to respond to the public through improved performance in health, safety and environmental quality. It is not a public relations program, but rather a performance-based program that requires constant interaction with the public, the government, employees, and every other person affected by our industry. While Product Stewardship is a code in the Responsible Care Program, Product Stewardship is apparent in all the codes of management practices.

You'll notice in the chart below that Product Stewardship is considered in each area of the product life cycle, from design to disposal. That means Product Stewardship responsibility lies with each and every employee along the life cycle of the product.

Codes of Management Practices and Product Life Cycle

CODES OF MANAGEMENT PRACTICES	PRODUCT LIFE CYCLE								
	Design	Develop	Manufacture	Transport	Sell	Use	Dispose		
Community Awareness & Emergency Response									
Process Safety	-				·				
Distribution		•							
Employee Health and Safety									
Pollution Prevention					·				
Product Stewardship				4					

Product Stewardship requires a total team effort. Marketing, Research and Development, Manufacturing, Quality Assurance and Distribution all must work together to provide the necessary commitment, support and resources for the Product Stewardship activities of each product. For example, Marketing furnishes customers and distributors with appropriate information to promote proper handling, use and storage of products. This information allows employees, customers and distributors to determine use limitations that may involve human or environmental hazards and to work with producers to address these issues through modifications to products and their uses.

Research and Development is responsible for conducting needed tests at each stage of product development to look for potential hazards. They also develop applications that permit the handling, use and disposal of products without creating an unacceptable level of risk. By providing information to production, distribution and marketing — employees, distributors and customers can learn proper product usage. R&D also re-evaluates the need for additional health, environmental and safety information as technology and regulations change.

Manufacturing reviews product specifications and assures that the work environment is considered when plants are designed, operating practices developed, processes changed and employees trained. They also inform employees about the product's physical make-up and consequences of overexposure. Manufacturing is also responsible for obtaining health information on products from suppliers. They furnish contractors with exposure guidelines, proper handling, use and disposal of products. It's also their job to adhere to pollution control and industrial hygiene standards and respond to local health and environmental concerns.

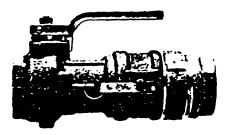
Quality Assurance is responsible for exactly that — assuring the quality of products and services and that the products are well documented and labeled in compliance with regulations. They also audit the performance of systems and processes to monitor conformance of policies and provide technical assistance in quality improvement programs.

Distribution determines that appropriate steps are taken to protect persons, property and environment while products are being transported and stored. They select the proper containers for distribution and the proper carriers, warehouses and terminals to perform distribution functions.

It's crucial to a good Product Stewardship program that each function of the product life cycle work together. It is a total team effort to pull together — and basically, it's a commitment among those functions to help develop the needed data and to work with customers to support the safe use of our products.

Let me give you a good example of commitment to Product Stewardship in a Research & Development function. We'll call the product steward in this example Carl. A major part of his job is Product Stewardship for allyl chloride and epichlorohydrin. When Carl was introducing Product Stewardship procedures to his customers, he ran into an awkward situation. A medium-sized chemical company in the Midwest ordered its first shipment of allyl chloride and Carl insisted on visiting the customer and inspecting the safety facilities before the shipment was delivered. Upon inspecting the facilities, it was discovered that the company didn't have safety showers within 25 feet of the delivery area. The customer promised the showers would be installed at a later date. But for safety's sake, the product steward insisted that the showers be installed before the delivery or the shipment would be stopped. Naturally, the customer was angry — at first. Then he realized that the product steward was putting the safety of his customers before the company's profit. He saw Carl in a whole new light.

Let me give you another example of commitment to Product Stewardship and customers. A product steward introduced his customers to a new innovation called a dry disconnect valve designed for the safe handling of allyl chloride and epichlorohydrin. When using this valve, only a few drops of the chemical would be lost from the hose during a tank truck unloading — as opposed to losing as much as a gallon with some conventional unloading systems. Again, customers were skeptical. They didn't think the valve would make a difference. After the first "dry run" testing of the valve at an unloading site, those skeptics became believers — very appreciative believers. This is just one example of how Product Stewardship is a means to prevent pollution.



THE BENEFITS OF PRODUCT STEWARDSHIP

Product Stewardship Programs can, if properly organized, protect people and the environment through pollution prevention, waste reduction and safety procedures. If each employee is dedicated to the Product Stewardship Program for their products, workers will be safer, chances of exposure and accidents may decrease and emissions may decrease.

Product Stewardship also helps protect products from misuse. As mentioned earlier, part of the program includes proper and specific labeling and handling instructions — and sometimes a trip to the customer's location to review storage, safety and even disposal facilities. All of these are good methods for preventing not only pollution, but misuse of the product. When products are being used accurately and according to your Product Stewardship program, chances of liability and exposure to adverse publicity are greatly reduced.

THE PROVISIONS OF PRODUCT STEWARDSHIP

Product Stewardship can help show an increase in product safety and assessment. It promotes proper use of products and provides adequate and clear warnings that customers should be aware of. If your company currently has a Product Stewardship program, but it's basically internal, perhaps you may want to extend it to your customers. This means notifying customers of any new hazard findings either from the environmental, TOX or use standpoint — and giving customers various forms of information to help them with product disposal problems. In some cases, it may even mean prohibiting the use of your products in certain applications.

Customer Support

After customers learn what we're trying to accomplish through Product Stewardship and that it promotes their safety, we've found them to be overwhelmingly supportive. Customers do read and appreciate the safety and handling information. And they're always looking for information about regulatory and compliance issues. Regulatory information isn't always easy to understand and customers appreciate the help in addressing its requirements. Understanding of the regulations allows customers to more easily incorporate changes into their everyday processes — changes that keep them in regulatory compliance, prevent pollution and control waste.

PRODUCT STEWARDS

Ideally, every product manufactured should have a product steward to follow the use and distribution of that product. Product stewards are expected to be experts on the chemicals they are responsible for.

Responsibilities

Product Stewards are also expected to:

- · teach others about chemicals
- respond to emergencies
- know and interpret material safety data sheets and labels
- review customer facilities
- give technical information
- know the laws and regulations for their chemicals
- help customers address product handling deficiencies
- evaluate customer uses of the product and consider potential risk
- participate in product safety reviews (PSRs), and
- know and work with resource specialists TOX, environmental, industrial hygiene

Knowledge Required

It's important that product stewards keep up with significant new information and communicate it to customers. It's also their responsibility to provide health and safety information on their product. That may mean training internal employees or customers about the product. Product stewards need to be aware of the ongoing evaluation of the use, storage and disposal of products; if there will be future stewardship requirements or additions placed on that program. They also must communicate changes in brochures, literature or technical data sheets, help in the evaluation of the regulatory impact, and initiate corrective actions.

In addition, product stewards need to know about the chemical, physical and biological properties of the product. They must know the mode of distribution into commerce, whether direct or through a distributor, and whether it's a mixed shipment. Customer storage facilities must be adequate. Product stewards should know of other materials in storage and their location. It's also important that they know how the product will be used by the customer. Are the customers considered high- or low-technology companies? And what will be needed to help them use your products safely? What about disposal? How much of the material is unused? Is it localized or general? If they incinerate, which products? Are there any recycling or reclamation programs in effect? What programs are available for correct disposal? A product steward must know answers to all of these questions to better help employees and the customer.

Customer Assistance

The amount of assistance a product steward may give a customer depends on the sophistication of the customers and the hazard properties of the product. Some product stewards will devote 5% of their stewardship responsibilities, some will give 25% of their time and some will give 100% of their time. It just depends on the nature of their product, the uses, and the customer base they support.

Product safety reviews should be an active part of your Product Stewardship program. Each product should go through a product safety review to ensure that appropriate steps are being taken to protect employees, public health and the environment. The product steward would help organize and conduct the review process, which includes manufacturing, marketing, legal and toxicology. These reviews can be done in various stages of product development and, certainly, if an unexpected incident arises or if new data comes along that affects health and the environment.

A Product Stewardship program can offer customer support and assistance in the form of industrial hygiene surveys; safety training using literature, posters, usage presentations and videos; and discussions on material safety data sheets. You can also provide information on loading and unloading of the product, waste reduction, reclamation, and disposal and regulatory assistance. All of this information will help your customers learn to use your products safely and effectively.

At Dow, we've had over 20 years to refine our procedures and support programs. Continuous improvement is a daily occurrence. Your Product Stewardship program doesn't have to be this in-depth. It can and will develop as your needs grow and as your company sees the benefits from Product Stewardship.

HOW TO ENCOURAGE EMPLOYEES TO COMMIT TO A PRODUCT STEWARDSHIP PROGRAM

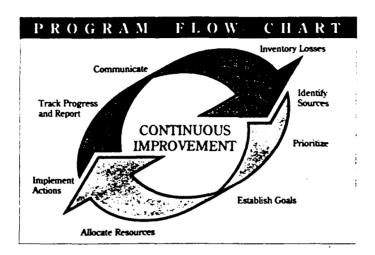
As mentioned, some companies may have Product Stewardship programs in different stages of development. That's great. The point is, everybody should have some type of a Product Stewardship program — for the good of your company, your customers and the environment.

Incorporating a program into your company will help prevent pollution, reduce waste, assist in regulatory compliance and possibly increase business. But how do you get your employees to buy into it? After all, the success of a Product Stewardship program relies heavily on employee commitment and participation. One method we used to get employees interested involves a new waste reduction program called WRAP — which is an acronym for Waste Reduction Always Pays. WRAP has five goals:

- 1. reduce waste to the environment
- 2. recognize excellence
- 3. enhance waste reduction mentality
- 4. measure and track progress, and
- 5. reduce long-term cost.

Each of our manufacturing divisions is responsible for the development and implementation of the WRAP program within its own operations. This allows each division the flexibility to tailor the program to specific needs. Each division is also responsible to encourage employees to take a proactive role in reducing waste and committing to continuous improvement through Product Stewardship. Encouragement methods used include idea-generating contests, utilization of quality performance techniques, plant waste reduction reviews, recognition/reward programs and even the development and communication of top ten generator lists for waste and emissions at a division.

Waste data — which includes emissions — is collected across all media, by process, at a facility. A ratio of waste versus production is then calculated to account for production variances. The waste ratio or index can be tracked and evaluated by each facility. The program flow chart lists the steps taken in the WRAP process to achieve continuous improvement.



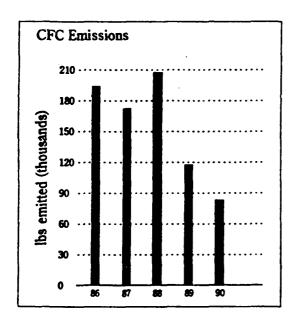
Each plant is asked to develop an inventory of its waste streams that may affect the air, water or land. Specific waste streams are identified and researched as to how they are produced by the process. They are then prioritized for further investigation and action based on volume and toxicity concerns. Tracking progress is fundamental in monitoring the impact of the plant's efforts. It also allows the facility to communicate its performance to employees and the community.

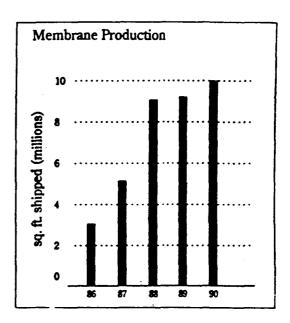
Since 1974, our plants in the U.S. have cut air emissions by more than 85 percent. And we continue to strive for further improvements. Although waste reduction sometimes requires capital improvements such as new equipment and upgraded facilities — many of the waste reduction projects have ended up saving us money. We've saved money on feedstock costs, waste treatment and on landfill costs. And in many cases, we've also increased productivity and improved product quality.

Examples of How WRAP Works

Here are a few examples of how successful our WRAP program has been. In one department for films, a waste reduction team identified ways to improve the manufacture of barrier films through source reduction and improved quality control. The team made equipment modifications including: modification to a film winder for operation consistency, which reduced the amount of rejected material; new gauging equipment to minimize thickness variation, which further reduced film rejection; new monitoring equipment to ensure that the resin is not overheated and therefore unusable; and a new roll-and-trim grinding system was installed to make pellets out of scrap material. The recycled product can be sold to recycle customers. The results yielded a 400,000 pound a year reduction in materials going to landfills, and a cost savings of \$100,000 a year. The addition of the roll grinding system reduced landfill material by 100,000 pounds a year, at a savings of \$30,000 a year.

At one of our plants, a waste reduction team identified an opportunity to reduce CFC emissions from the manufacturing of membranes. These membranes are used in water purification systems and other systems that remove water from substances such as cheese. The team implemented a number of changes and modifications. Distillation equipment was installed to purify and recover unused liquid CFC from the process and a carbon absorptive system was installed to collect the CFC vapors, which were then sent back to the distillation equipment. In addition, specialized equipment was installed to remove water from the recovered CFC so it could be reused. Later, neutralizing and collection tanks were installed to reclaim more CFC for reuse and existing equipment was upgraded to improve process controls.





As a result of these waste reduction steps, the plant reduced the amount of CFC emissions by 87 percent since 1986, saving over \$1.6 million. Also, membrane production more than tripled over that same time period.

CONCLUSION

The examples I've given are part of our WRAP program, which is part of our Product Stewardship program. We've been working toward improving our operations for years — and that's basically how the Product Stewardship program evolved. Product Stewardship has also helped us comply with government and EPA regulations. For example, through our commitment to Product Stewardship, we were anxious to participate in the EPA's 33/50 program. The 33/50 program is the EPA's voluntary pollution prevention initiative to reduce national pollution releases and off-site transfers by 50% in 1995. The interim goal was to reduce releases by 33% in 1992. With a strong Product Stewardship Program in operation, sometimes we're in compliance before the regulations are even issued. That's just better for everyone.

To close, I'd like to emphasize the importance of Product Stewardship to your company, to your customers and to our earth. If we don't commit now to pollution prevention, waste reduction and recycling — all aspects of Product Stewardship — then we can expect a more expensive and harsh commitment in the future. Now is the time to make the investments needed to ensure that future generations will continue to use our products — safely and effectively.

Experience has shown that customers want to do the right thing. They use safety information and want to comply with regulations. As suppliers of these products, it's our responsibility to help our customers understand the regulations and how to comply with them. That's Product Stewardship — an investment of our resources, our time, and our capabilities in the whole product life cycle. It's knowing the full capability of our products and explaining those capabilities to the users.

Conferences like the Pollution Prevention Conference give us the opportunity to cooperate, learn from and work with each other as an industry. We have the opportunity to discuss regulations and compliance so we can take a proactive approach to making our businesses as safe as they can be — for our workers, our customers, our communities and our Environment.

SESSION 6

INORGANIC COATINGS

PAPERS PRESENTED:

"Long-Term Corrosion Protection with Single-Coat, High-Ratio Zinc Silicate"

bν

Parke Schaffer, Jr.

Inorganic Coatings, Inc.

Malvern, Pennsylvania

"Two Surprises from Inorganic Zinc-Rich Silicate Coating A reactive semiconductor approach to surface protection"

bν

C. William Anderson

Marine Environmental Research

Morehead City, North Carolina

"A New Inorganic Coating for Magnesium Alloys with Superior Corrosion Resistance"

by

Alex J. Zozulin

Technology Applications Group, Inc.

Grand Forks, North Dakota

and

Duane E. Bartak

University of Northern Iowa

Cedar Falls, Iowa

"Inorganic Chemistry as an Option for Formulating High Solids, Low- and Zero-VOC Architectural, and Industrial Maintenance Coatings"

D)

Christine Stanley

Raymond E. Foscante

Ameron

Protective Coatings Division

Brea, California

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

Long Term Corrosion Protection with Single-Coat High-Ratio Zinc Silicate Parke Schaffer, Jr. (Inorganic Coating, Inc.)

Today I will be talking about water-based zinc silicate, follow its evolution from the early 1940's to the present; the evolution from post-cure and self-cure products to the no-cure high-ratio, NASA formula that is available today.

Water-base zinc silicates were first developed back in the 1930's, but the first large commercial application was in 1942 on the Wyalla pipeline -- a 250-mile pipeline stretching from Wyalla to Morgan in Australia. The pipeline runs through the desert, through salt marshes and along the coast within a few yards of the ocean. After 48 years of exposure, a single 3 mil coat of water-base zinc silicate is still protecting the pipe with no sign of breakdown.

That first application of zinc silicate in 1942 had a unique curing process. The product was applied and then baked at about 450°F to cure out the alkali metal that is present in all silicates. In the early 1950's, the product was brought to this country and a post-cure acid wash was developed to cure or neutralize the alkali.

(The following slides detail long term applications of post-cure and self-cure zinc silicates.)

In order to understand how any coating could protect steel permanently, it is important to understand the basic corrosion process on steel.

(The following is a discussion with slides, detailing the corrosion process on steel.)

There are three basic ways to stop corrosion:

- 1. With organic barrier coatings such as epoxy, urethane, acrylic, vinyl, etc. Barrier coatings adhere by means of a mechanical bond (vs a chemical bond) and because they are organic, break down over time.
- 2. By galvanizing or metalizing with pure zinc metal applied to the steel surface. A pure zinc coating protects by setting up a new anode/cathode relationship with the steel acting as the cathode and the zinc sacrificing as the anode. In mild environments this sacrificial method may last 40 years, however, in an extreme acid rain, road salt or marine environment, the zinc will sacrifice rapidly. When the zinc is depleted, corrosion will begin.

3. Or a third means of controlling corrosion is by applying a single coat of water-base zinc silicate. Both the above principles are at work with zinc silicate since it first acts galvanically or sacrifically and finally becomes a permanent barrier coating. Here's how it works:

Zinc silicate is 90 percent zinc and 10 percent silicate or liquid glass with the active componant being SiO₂ or silicone dioxide. SiO₂ has the unique capability to chemically complex with metal. The 90 percent zinc content initially sets up the same anode/cathode relationship as in galvanizing but with one major difference. The zinc oxides formed by the sacrificing zinc continue to react with the SiO₂ while filling the pores in the porous film. Over time, the oxides form an extremely dense hard coating that ultimately seals off to become a permanent barrier coating. Why permanent? Because the backbone of the coating is ceramic, or glass, or SiO₂, that is chemically bonded to the iron on the surface (over 2000 PSI). It does not break down over time.

(Many slides -- graphics and actual cross sections -- will be shown to illustrate all of the above; other slides will illustrate the self-healing properties of zinc silicates.)

So far, we have seen how generic zinc silicates protect steel and while all zinc silicates work in the same way, there has been a definite evolution in silicate chemistry that has allowed quality and production advantages.

In order to understand the evolution from low ratio post-cure and self-cure to high-ratio nocure, you must understand the basic chemistry of alkali metal silicates. (Slides will aid in the following discussion.) Water-base zinc silicates are, very simply, silicate and zinc. And silicate is liquid glass. The question has been asked many times, "How is it possible to make glass into a liquid since glass is insoluble?" Chemically, SiO_2 and water will not react and might be illustrated by: $SiO_2 \parallel H_2O$. However, if you will recall, early in this discussion I mentioned that SiO_2 reacts chemically with metal -- so if we can identify a metal that holds or reacts with water, we could bridge the SiO_2 and H_2O . The alkali metals, sodium (Na) potassium (K) and lithuim After application of a standard ratio (3.75:1) zinc silicate, it's the alkali that must be cured out of the zinc silicate film. The solublizing agent must be removed by one of three curing methods: high temperature or baking, acid wash port-cure, or long term self-cure. It is this curing requirement that has kept water-base zinc silicates in a small niche market. In the early 1970's, NASA undertook a program to solve the curing problems and take advantage of the chemistry's permanent protection.

NASA found a way to raise the ratio from 3.75:1 up to 5.3:1 -- in other words, they found a way to remove the potassium metal before it goes in the pail, while maintaining the stability of the high-ratio liquid glass. So the curing process for high-ratio zinc silicate is simply evaporation of the water. As the water evaporates, the high-ratio film becomes insoluble and extremely hard and adhesive reaching 1000 PSI pull strength in just two hours.

The high-ratio chemistry now allows the easy application of a water-base zinc silicate without a post-cure or indeterminate, lengthy self-cure. Additional advantages include:

recoatable with itself for additional millage or easy repair; self-inspecting over organic contamination; mudcrack and overspray resistant up to 6-8 mils DFT; topcoat with epoxy, acrylic, etc. in two hours or less; zero VOC's, no fire hazard, no toxic chemical waste; unbeatable economics, both short and long term.

(Following will be slides detailing long term and application case histories which illustrate the permanence and above advantages.)

The high-ratio zinc silicate NASA formula provides permanent protection with just a single coat. Permanent protection, coupled with the advantages above, offer short and long term economics that are beyond comparison with any coating chemistry that has come before. High-ratio zinc silicate chemistry is destined to become the world standard in corrosion protection for steel.

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

TWO SURPRISES FROM INORGANIC ZINC-RICH SILICATE COATING

A reactive semiconductor approach to surface protection

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Introduction

Much of the information we are seeing at this symposium revolves around the utility of Zn rich coatings. Marine Environmental Research (MER) has been examining these coatings as the material component in a surface protective system applicable to both marine and land based needs. The non-material component of this system is electrical. The way these two components interact and the surprising results are addressed in this paper.

Pushing an object through a fluid seems a simple enough system to model. It is simple until an attempt is made to do so. Recent Americas Cup races have been decided on the basis of who has the best modeling software. Military and commercial operations spend a great deal of effort approaching this problem. In general, the resistance to pushing objects through water can be treated as having two components: static and frictional. Static resistance is predominantly a function of the shape of the vessel and is most important at higher velocities (surprise). Frictional resistance is determined largely by the "roughness" of the vessel hull surfaces. How important this can be is shown in figure 1.

These diagrams show that is possible to quickly require increased fuel burning just to keep the same speed. Since shipping is based on meeting timetables and not consumption tables, biofouling that results in an increased roughness of vessel surfaces is a major concern of marine traders. Power requirements rise, vessel ranges drop and the new limitations hinder commerce and defense. Over the years, methods have been put forth to keep fouling to a minimum.

Efforts at keeping the hulls clean include scraping and antifouling coatings. The antifouling coatings have included copper, tar/pitch, coatings with toxic components and coatings that are ablative, hard or slippery(1). Figure 2 shows this schematically. None of the existing systems are suitable for large scale commercial applications for reasons of cost, environmental concern or longevity.

Body

Since the interface between any surface and ion containing solution (like seawater) has an inherently electrochemical character, it made sense to examine an antifouling approach that utilized both electrical and chemical properties of this interface (see figure 3). William J. Riffe began a series of field and laboratory experiments combining conducting or ionic coatings and impressed electrical signals. After a decade of constant experimentation, he had found an incredibly effective antifouling system: inorganic Zn rich paint and pulsed electrical signals.

The MER antifouling system consists of two components: a Zn rich inorganic coating and an electrical signal. The Zn rich coating is applied to the surface utilizing common application technology. A coating thickness of a few mils is sufficient and can be conveniently applied in one or two passes by a single operator with minimal time between coats. The lack of volatile solvents or other transference agents reduces the occupational and environmental impact of application. Low Zn leach rates both extend the useful life and lower environmental concerns while the system is in use. Several of the physical properties of the inorganic Zn coating component of the MER system are those expected of the coating itself. The color, hardness and surface smoothness of the coating are just what is expected for comparable inorganic zinc coatings. The behavior of the coating changes substantially under the influence

of electrical modulation, though.

The electrochemical component of the MER antifouling system is the non-classical approach to the antifouling problem. Zn rich inorganic coatings have significant conductivity and can be thought of as a complex and heterogeneous electrode surface. An applied potential of appropriate value is able to allow the controlled release of Zn^{2+} ions into the solution immediately in contact with the coated substrate. Milliseconds later, reversing the electrochemical perturbation results in the replating of the Zn^{2+} ions as Zn° back in the coating where it originated. Replating efficiencies for metal ions stripped from 7 micron diameter electrodes (the diameter of the average dust particle in our formulation) in potential pulse experiments can rise over 99.95% This results in virtually no net loss of Zn to the surrounding solution, yet allows some Zn ions to be present in the solution just at the surface at intervals sufficiently frequent to deter barnacle larvae and other species from adhering to the underlying substrate. This represents a major advance in antifouling technology from cost, application, environmental and longevity standpoints.

When evaluating the electrical/electrochemical component of this system, several questions became evident. While the first experiments were able to produce a significant antifouling system, it wasn't clear what the pertinent electrochemical variables were. If you are trying to optimize a process, it is reasonable to have a clue about what variables you wish to adjust. A series of experiments were undertaken to determine if current, charge, potential or frequency were the principal electrical parameters.

The initial suspicion was that the charge placed on the surface of the coated surface was the principal antifouling action factor. The understanding of the solution-electrode interface given by the Gouy-Chapman-Stern etc. models revolves around the capacitive and faradaic behavior of the interface (2). Electrons present on the surface of a conductor with insufficient energy to be transferred to orbitals on solution species will still attract cations in the solution. These cations then form a layer of charge adjacent to the conductor. These two layers of charge form a capacitor. Counterions extend further into the solution. This series of charges and ions is called the electrochemical double layer and gives the electrode-solution interface many of its observed properties.

The first significant event in the process of attachment of biofoulants to a surface involves a "glue" protein, a charged polymer produced by fouling organisms. Macromolecular charges play a significant role in their structure, migration and orientation with respect to other substances. Since ionic interactions can be critical in the establishment of an attachment of biological species to surfaces, it made sense to attempt to modulate the charged double-layer in hopes of disrupting the "glue" - surface attraction, thereby creating a deterrent to biofoulants. The first experiments were conducted with a current path directed between the vessel hull, through the Zn coating to external anodes, cathodes or the surrounding ocean. Examination of the current-charge transients for potential pulses showed very small current passage through the coating and a dominance of capacitive over faradaic charge transfer. That finding had two implications. Any redox processes that resulted in mass transfer between phases were minor and the capacitive component of the interface was important.

Upon examining the antifouling mechanism, it became clear that the Zn had profound effects on larval metabolism (especially on the glue production) in barnacles and that the nature of the applied electrical pulse sequence changed both antifouling characteristics and the current time transients. Surfaces coated with the inorganic Zn coating and subjected to a pulsed electrical signal remained largely free from hard fouling and those few barnacles that were able to attach to the surface were so loosely held that they could be swept off with a wipe by a hand. The inorganic Zn coating appeared to have some "odd" capacitive behavior, as well.

By coupling the coating (ca 90% Zn, ZnO and 10% silicate binder) with an electrical pulse, significant antifouling capability is produced that can last for years in service. The current requirement for antifouling action is minuscule: 100 foot long vessels require only standard car battery sized supplies, for example. Vessels, even stationary in the docks, remain largely free of hard fouling for years. Those few barnacles that do manage to stick are held so loosely that a swipe of the hand will dislodge them.

A Test

These findings were brought together and tested on a system where fouling was becoming a significant problem: electrical power plants. Zebra mussels and other biofoulants were beginning to clog even the huge heat exchanger water supply "pipes". Shut down and cleaning the heat exchangers can be incredibly costly, upwards of \$1 million per day, simply on the basis of lost generating capacity. As a part of a major study of potential antifouling coatings, Drs. Leitch and Puzzuoli at Ontario Hydro examined the MER inorganic Zn system (3) and thirteen other coatings for their antifouling characteristics against zebra mussels. When the MER inorganic Zn system was installed on a set of flags (coupons or panels) near power plant heat exchanger intakes, protection against zebra mussel biofouling was provided. Two years later, the remaining intact unit continues to provide protection. MER's inorganic zinc coating system (both physical and electrical) was the only non-silicone coating demonstrated as effective against the zebra mussel fouling. The MER system showed only a few percent of the fouling present in the control experiments. Identical units treated in the same manner in the same study suffered the disconnection of the electrical signal source. Those units are beginning to show signs of fouling: this is in the field confirmation that both the coating and the electrical signal are required to give the indicated antifouling character.

Subsequent experiments showed that it was not required to have the bulk of the current flow go from inside the supporting structure into the surrounding solution. Simply passing a current through the underlying conductor structure imparted antifouling protection to the surface. We believe the mechanism of action is the same in this configuration, only that current leaked across the interface gives the required Zn ion.

Tests on small stationary vessels, larger commercial tugs and industrial power plant installations show the MER inorganic zinc - electrical system to provide effective antifouling for years in the rather extreme marine environment. But that's not what we want to address here.

There are two competing aspects a new technology: performance and theory. As we all develop new technologies, we gain experience in the models and theories of that technology's operation. That normally gives us the idea, based on some theoretical grounds that a particular behavior is possible within a technology. As we approach the development of the new idea, we have some theoretical basis for our approach. Before others invest any time, effort or money, the following question is asked: "We see that there is some theoretical evidence for this technology, but does it actually work in the field?" On the other hand, and less frequently, we find some interesting technology that we actually observe in the field. This time, when we try to develop the technology, we are asked: "We see that it does actually work in the field, but is there some theoretical evidence for this technology?" This is the situation MER was in: we had an observable process, yet not a clear underlying theoretical basis for its operation. Experiments were conducted to try to correct this situation.

The nature of the specific experiments conducted is not entirely pertinent to this discussion, but during the course of examining the antifouling mechanism, two critical observations were made:

- 1) Zn was the active component in the antifouling action and the electrical signal significantly prolonged the lifetime of the efficacy of the coating.
- 2) In some installations, the underlying support for the coating showed substantial structural integrity, far beyond that expected under the circumstances.

A third piece of evidence came in at the same time: Zinc leach test results. Antifouling agents have been notoriously harsh on the non-fouling biological systems living near places where marine vessels spent any significant time. In order to assess the localized potential environmental impact, zinc leach rate tests were

conducted (EPA test SW-846) and showed MER's inorganic zinc coating formulation has a sub-ppm Zn/day/M² covered surface leach rate. While this is a thousand-fold lower than that found for the zinc dust alone, the relatively impervious crosslinked silicate binder should effectively shut down much ion and solvent movement so the lower zinc leach rate is expected. The incredibly low Zn leach rate, the structural integrity of the underlying steel matrix and the prolonged lifetime of the antifouling (due to Zn) action suggested that the MER coating system would have significant effect as an anticorrosive coating system. Again, The MER system relies on both a material component (the inorganic Zn coating) and an electrical component (the electrical signal). Antifouling action was significantly enhanced and prolonged with the application of the electrical component. Since Zn ions are the active agent, the electrical signal appears to help retain zinc in the coating.

With some simple calculations, it is possible to predict a useful lifetime for MER's coating system: at a coverage of 60 microns, 0.5 microns of the Zn would leach into solution per year. That extrapolates to greater than 100 years. The use of this coating system above the sea, on "dry" land would only serve to reduce the rate of Zn leaching, stabilize the material part of the system and provide longer than expected lifetime. In fact, we know that the entire underlaying substructure is not protected until the last bit of inorganic zinc coating is gone. Localized deterioration may occur. Even so, at this point, there is likelihood that this coating system (both material and electrical) will provide anticorrosion protection beyond the lifetime of those applying the coating on the structure. Considering leaching solely, 75-125 year effective lifetime is not out of the question at this point.

And now, the hard part: elucidation of a mechanism of action.

Before continuing, it is useful to examine the current model of corrosion and some attacks that have proven successful in the slowing of corrosion processes. We will begin with considering the electrochemical cell and then the corrosion process cell analog. Figure 4 shows a standard electrochemical cell. The chemical half reactions in the left and right portions of the cell transfer electrons externally to the solution through a conductor. The anode electrode is the corroding substance of interest. As metal atoms ionize, the ions are either dissolved in the solution or form ionic surface compounds on the anode. Figure 5 focuses on the local cathodic region of a metal protected by inorganic Zn coating. An oxidant, usually water or water related, is reduced at the cathode to form gases (like Hydrogen) and other charged species. Charge is carried between the two electrodes through the solution by ionic transport mechanisms to complete the electrical circuit.

Virtually all anticorrosion strategies focus on one area of this complete process. Alloying strategies address either conductivity within the metal or the electron transfer process at the electrode solution interface. Prophylactic insulating coatings attempt to interrupt the interfacial electron transfer by providing a barrier to reactant approach. Simply keeping the surroundings "dry" can impede the charge transfer between anode region and cathode region through the surroundings, as well as lowering the concentration of the reactant at the cathode. Cathodic protection by sacrificial anode "short-circuits" the process by providing a better route for electrons that eventually show up at the cathode. Every electron (or two) that doesn't come from the original anode means there is one more substrate metal atom that didn't oxidize.

Since both antifouling and anticorrosion are within areas where Zn has found some use, we looked first to models of operation that zinc has clearly exhibited in the past. This lead us to amass a list of what is NOT going on in this system:

First (and perhaps most important) is that the MER system doesn't appear to function utilizing zinc as a sacrificial anode. The loss of zinc from the surface matrix is minuscule, as shown by the leaching tests. Field tests also support this position. We will see more about this later.

Secondly, this system isn't operating by cathodic protection. The magnitude of current - potential - charge that is employed in this system is microscopic compared to the normal values found in cathodic protection (4). Typically, tens of mA/square meter are used in cathodic protection of galvanized steel.

MER's system operates on tens of microamps per square meter. In fact, it was in the experimentation related to assessing cathodic protection as a mechanism that we noticed that the capacitance associated with the solution - coating interface was not even close to that expected. Higher than expected capacitance jumped out to us as well as a dependence of capacitance on potential. Differential capacitance is nothing new but we felt that the variation was larger than we expected.

Thirdly, the system doesn't behave as a simple insulating impervious coating. The measured resistance through the inorganic zinc coating is too small. A typical 200 micron coating of MER's cured coating shows a resistivity of around 2×10^3 kilohms-cm. This is way too low to behave as an effective insulative coating, yet not low enough to be a "good" conductor.

One more aspect of the MER inorganic zinc coating not yet mentioned is the rough physical composition.

As we examine the materials that comprise the coating, the several percent of the coating that is NOT zinc metal looms large. The few percent of the matrix that is silicate based will have substantial network silicate structure after the curing and crosslinking of the coating removes carrier and expelled reaction product water. The remaining crosslinked network will have largely insulator characteristics (5). The zinc metal, of course is a reasonable conductor or at least a very good p-type semiconductor and has found use in chip gate manufacture. It is reasonable to imagine Zn as a gate material in these applications, since it is viewed as a "p-metal". "p-metals" are those having hole mobility larger than electron mobility, as measured by the Hall effect. Thus, Zn can be thought of as having the character of a p-semiconductor (6). Finally, we have the few percent of the "zinc" that is actually zinc oxide. Zinc oxide in these films is at best, a heterogeneous phase, coating the zinc metal particles. During the application of the coating, some of the coating will undoubtedly be pushed aside and allow direct Zn-Zn contact between dust particles, but the particles will largely be coated with oxide of variable composition. The electrical properties of ZnO are interesting and complex. ZnO will act as a semiconductor with about a 3.2 eV band gap (7). Dopants or other compositional variations significantly alter the conductivity of ZnO, allowing resistivities of relatively "pure" ZnO from 10¹⁵ to 10⁻³ ohm-cm (8). This range spans resistivities of insulator and semiconductor materials. Assessing the electrical behavior of the MER coating system becomes problematic when we look at the incredibly low currents / charge needed for anticorrosive protection. The standard models for anticorrosion protection don't do well. The model we wish to present here is based on interruption of the electron transfer between metal substructure and the surrounding species. We believe the Zn / ZnO / SiO_x structure is behaving like a semiconductor device, and perhaps more specifically, like a Field Effect Transistor (FET). Perhaps more appropriately, it behaves like many FETs connected in several arrangements throughout the coating.

The FET structure

If we look at the model for a FET, and we will use a Junction FET (JFET) to illustrate the point, we can interpret portions of the coating structure in semiconductor terms. In the JFET case (figure 6), the charge transfer from the source to the drain must pass through a narrow region of semiconductor near the gate. As an appropriate potential/charge is placed on the gate, the nearby majority charge carriers in the channel semiconductor are depleted from the region around the gate. As the depletion region grows, the crossectional area available for majority charge carriers to move from source to drain drops. The source-drain current is lowered as the depleted region grows. When enough charge is placed on the gate, the conduction channel is finally "pinched off" and current flow stops. This is the classic way that JFETs can behave as switches, interrupting the flow of current from source to drain. Typical common-source forward transconductance (the relationship between gate control voltage and source-drain current) for a JFET is 10,000 micromhos. Small voltages control large currents. This effect is at the center of the use of FETs in amplifiers.

If we view the corrosion current as the source-drain current, then we can imagine controlling the magnitude of that current by the application of a small voltage/charge on the gate. We can model much

of the JFET from the components of MER's inorganic Zn coating matrix (figures 7 and 8). The cathodic portion of a corrosion cell would represent the source of electron flow. The redox processes provide V_{ds} . This voltage comes from a combination of submetal through coating to the surrounding oxidant or simply within the coating itself as some Zn metal is sacrificed. These electrons pass through the coating. With ZnO behaving as the n-type semiconductor, it would be analogous to the channel semiconductor in the above illustration. Since the typical ZnO layer is only a fraction of a micron thick, the interfacial region between two "Zn" dust particles would be thin enough to pinch off readily, shutting down charge transfer through the ZnO. The field drives the charge carrier motion and with a thin ZnO layer, the field for even a small potential drop will be large.

Since the drain would be the interfacial region between ZnO surface and surrounding oxidant, addressing the charge transfer through the ZnO layer and not the Zn dust. In fact, the electron transfer between surface and oxidant will necessarily involve electron travel through the ZnO layer.

Typical FET gate control voltages require 3-5 V to deplete the channel region. In the absence of leak pathways, the structure can remain depleted for a long time. In a typical MER application, there will be dozens to hundreds of particle-particle interfaces. There will also be particles that have metalmetal contact with other particles and base metal due to application force scraping away ZnO on impact. This means that the overall structure would less be modelled as a single FET, but as a series of FETs, each connected through a network of other FETs. This type of structure will likely be "leaky", requiring some redepletion in order to maintain the effect. The critical junctions, though, are those at or near the surroundings / coating interface. Interpreting the coating in terms of its semiconductor properties does allow us to address some of the observed anticorrosive action of the MER coating system.

- 1) Small charges/currents/voltages can control corrosion currents.
- 2) Cathodic protection need not play a role in this mechanism, yet electrical control is required.

 -the oxidation of the Zn in the coating can be very slow, as long as the gates pinch off the current through the ZnO channels.

Up to now, we have not addressed the presence of the silicate binder. The silicate binder need play no role in this model, but in fact it may contribute significantly. For example, if we include the (post-curing) silicate network insulating structures, a more appropriate model FET may be the Insulated Gate FET (IGFET) or the Metal Oxide Semiconductor (MOSFET). In these structures, the gates are electronically insulated from the substructure channel semiconductor. The depletion mechanism is similar to that for the JFET, in that a pinch off region lowers the charge movement through an underlying semiconductor channel. By this model, reducing the corrosion current by a factor of only 5 would extend the life of the coating by a factor of 5. This would turn a 8-year inorganic Zn coating into a 40-year coat lifetime, neglecting non-corrosion deterioration.

Utilizing semiconductor technology as a means to control is not new (9,10), yet the principal approaches have centered on modifying conduction band energies to inhibit electron transfer and not shut down current through external depletion of charge carriers. Some experimental evidence does support a semiconductor model approach to the MER coating anticorrosion system. For example, the pn junction has an inherent capacitance and that capacitance depends on the potential of the signal impressed across the junction. In addition, the resistance through these coatings is temperature dependent. At the temperature rises, the resistivity drops by about 1% per Kelvin over a range of room temperature to 40°C. Metallic conductor charge transport would show an increase in resistance with temperature. Semiconductor charge transport shows resistance drops as temperature rises. In fact, ionic charge transport shows resistance-temperature behavior similar to semiconductors in that respect and we are beginning experiments to discriminate between these potential mechanisms.

Conclusions

Inorganic zinc coatings are noted for their ease of application, low toxicity and wide applicability to substrates. MER has found two areas where a combination of inorganic zinc coating and impressed electrical signal results in significant prophylaxes.

Marine and freshwater antifouling protection is afforded by the MER coating system. The inorganic zinc coating and electrical signal are both required for optimum performance.

In addition, the MER system can provide anticorrosion protection for an extended period of time. The mode of action appears to involve the semiconductor nature of Zn/ZnO in the coating.

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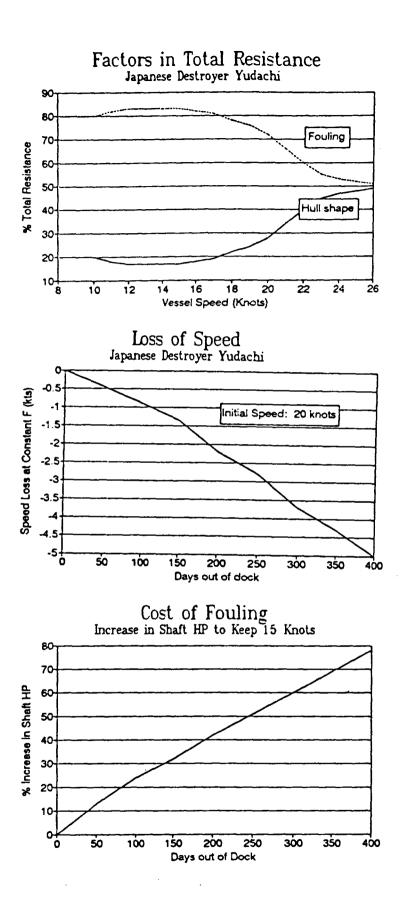


Figure 1. a) contributions of static and frictional resistance to the total resistance. b) loss of speed for a vessel kept at constant power as a result of increased fouling c) required power increase to keep a vessel at a constant speed, rising due to effects of fouling.

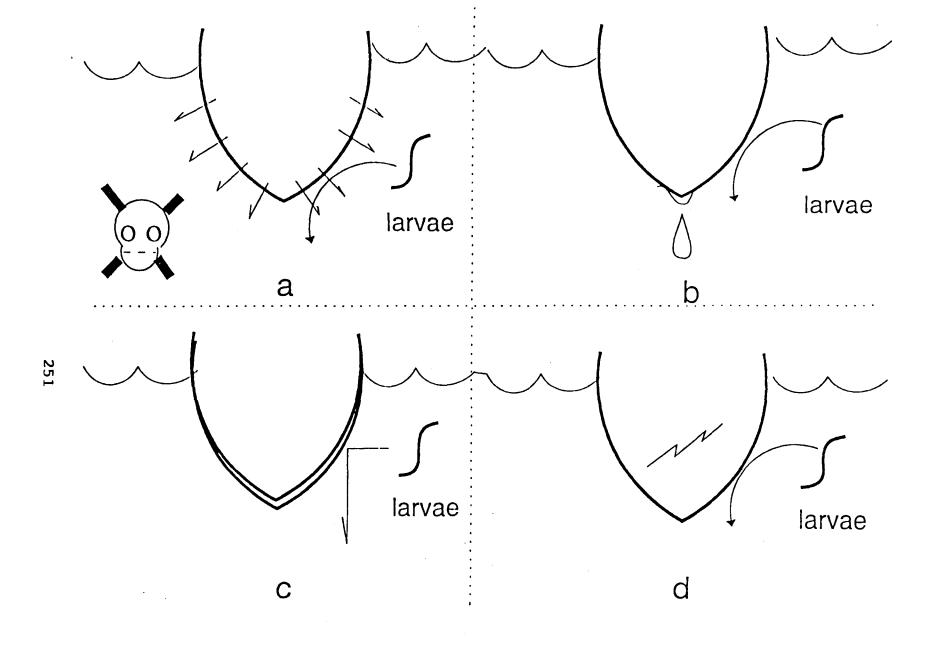


Figure 2. Four approaches to antifouling: a) toxic leaching b) ablative coating c) "hard" coating and d) the MER system.

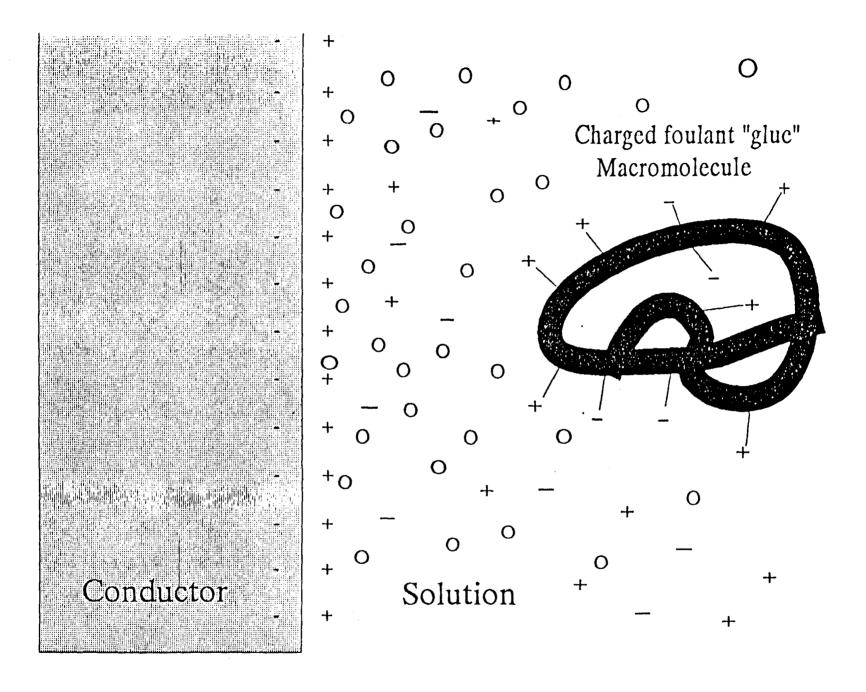


Figure 3. A primary event in fouling is the approach of the charged "glue" molecule to the surface to be settled on.

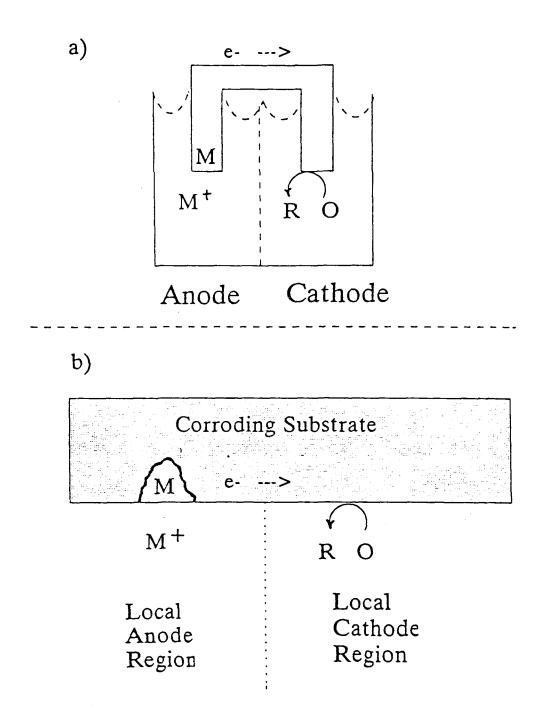


Figure 4. The electrochemical cell model for corrosion. a) a standard electrochemical cell, having separated half-cells b) a segment of a corroding substrate showing localized cells, with nearby anode and cathode on the same piece of metal. The circuit is completed by the movement of ions back to the region around the anode.

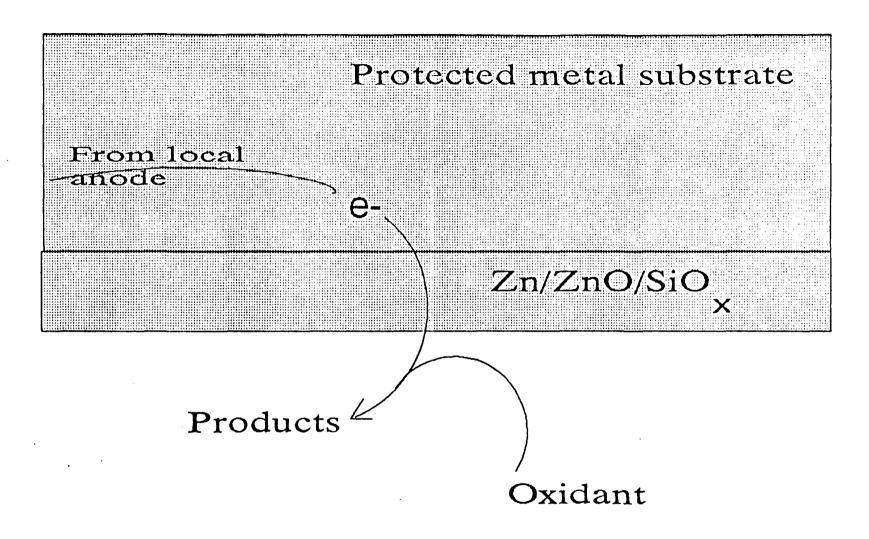


Figure 5. A view of only the local cathode region of a substrate covered with a protective inorganic Zn showing the path of current from a nearby anode region and out through the coating to the oxidant in the surroundings.

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JFET Operation

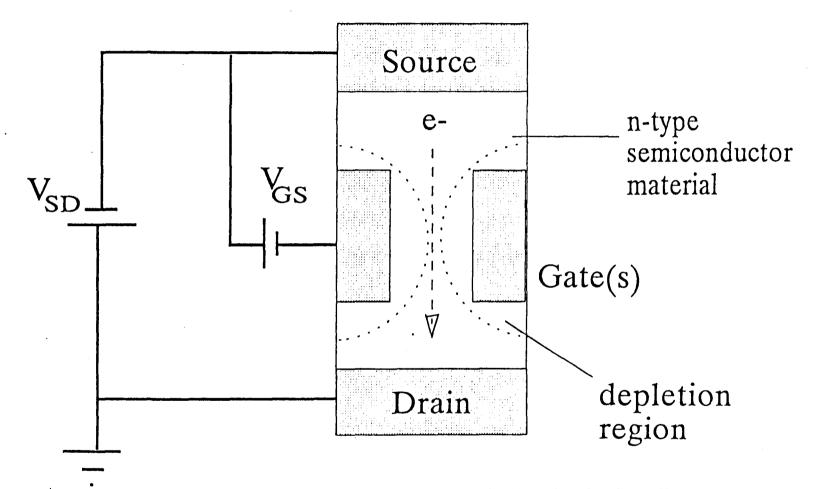
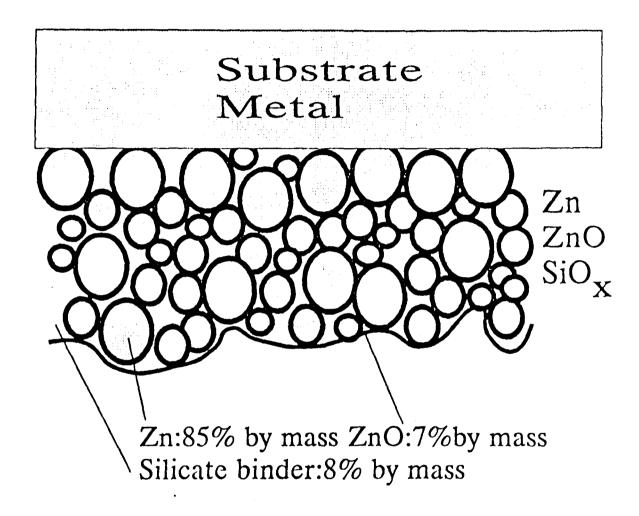


Figure 6. A diagram of the common mode of operation for a junction field effect transistor (JFET). Depleting the channel region of charge carriers reduces the ability of current to flow between the source and the drain.



(ca. 25 micron coat indicated)

Figure 7. If you were 500 microns tall, what would the surface and coating look like? This shows the coating a bit more to scale, with oxide layers present on the Zn particles and binder present. This coating would be about 1 mil thick.

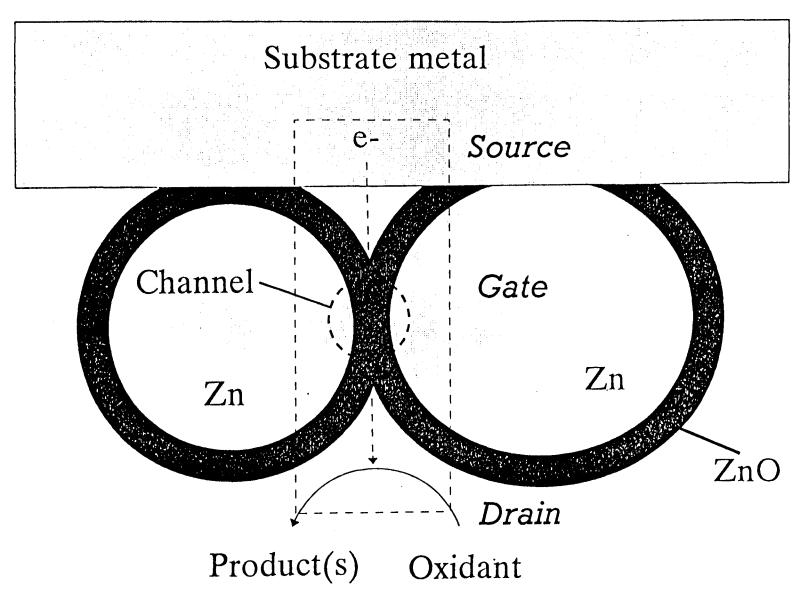


Figure 8. Focusing on a single pair of the dust particles in contact with the substrate metal, the analogous structures to a JFET appear: the source current comes from the reductant at the anode, the drain is the oxidant half reaction and the ZnO forms the n-type semiconductor channel between the gates. The externally applied signal provides the field to shut off the source-drain current.

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A New Inorganic Coating for Magnesium Alloys with Superior Corrosion Resistance

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INTRODUCTION

Magnesium, the sixth most abundant element in the earth's crust, is the lightest of all commonly used structural metals. Having a density of only 1.74 g/cm³, it is one and onehalf times lighter than aluminum, approximately four times lighter than zinc or steel and is comparable in weight to perhalogenated or mica and asbestos filled plastics. Although pure magnesium is too soft for structural use, the addition of other elements such as aluminum. zinc, manganese and rare earths have produced alloys with enhanced chemical and physical properties. Alloys of magnesium have found considerable use in applications where weight saving is important. The automotive industry has been looking increasingly towards magnesium for reducing vehicle weight, thus improving fuel economy, and is currently the major user of magnesium die cast parts. For example, a weight reduction of 125 lb. will yield a fuel economy improvement of 0.2 to 0.5 miles per gallon in the EPA Combined City-Highway test. In a recent perspective of magnesium in automobiles more than forty production applications of magnesium alloys on US cars are listed.² Other industries which benefit from magnesium's low weight include power tools, computers, recreational equipment and aerospace. In addition to it's low weight other advantageous properties include a high-strength-to-weight ratio, excellent dimensional stability, high impact resistance, good creep strength as well as high thermal and electrical conductivity. In addition, magnesium and its alloys are recyclable and present no toxicity hazard.³

Pure magnesium metal is a reactive metal and thus is easily oxidized. This oxidation or corrosion, galvanic as well as surface, is often the major obstacle against the use of magnesium in aggressive corrosive environments. However, through the use of high purity alloys with a low content of iron, nickel and copper, satisfactory performance may be achieved with respect to surface corrosion.^{4,5} For example, the corrosion rate in salt spray (ASTM B117) of high purity AZ91D⁶ and AM60⁷, both die cast alloys, range from 1-12 mpy and less than 20 mpy, respectively, while two sand cast alloys, AZ91E and WE43, exhibit similar rates of 5 mpy⁸ and 8-16 mpy⁹, respectively. Other commonly used alloys, such as ZE41A, demonstrate considerably higher corrosion rates. The corrosion rate of ZE41A has been reported to be greater than 400 mpy. 10 The utilization of these alloys, particularly in aggressive environments, will require the application of surface treatments to provide additional protection against surface corrosion. In contrast, alloy composition will have a limited influence on galvanic corrosion; however, in this case, the service performance will depend on the proper design, assembly and surface treatments as well as the metal purity.11 259

In terms of aerospace applications, magnesium alloys, including ZE41A, QE22A and AZ91E, are currently used to fabricate main transmission housings and other gear boxes for several helicopters which are used for commercial and military purposes. Other parts, which are cast using these alloys, include intakes and intermediate casing for aircraft engines, housing for auxiliary power units, canopy frames and speed brakes. In many cases, extremely corrosive environments are encountered and, as a result, high performance coatings are required to produce maximum protection against surface and galvanic corrosion while minimizing maintenance.

The surface treatment processes for magnesium alloys which serve as a paint base and a barrier towards corrosion can be grouped into two types. The first type is the chemical conversion coatings which are applied either by immersion, brush on or spray-type processes while the second type involves an electrochemical anodic process. Table I provides a list of the more commonly employed surface treatments. Though many of the conversion coatings do produce a surface that provides some corrosion protection and can act as a paint base, they are limited in applications on the more reactive sand cast alloys. In addition, the abrasion resistance of these coatings, including the anodic processes, are not particularly high. It is interesting to note that most of the treatments shown in Table I also utilize chromates in the primary coating or sealing bath. The utilization of chromates plus other materials such as cadmium, zinc, lead, copper and many volatile organic compounds (VOCs) has resulted in the EPA identifying the metal finishing industry as one of the most significant contributors to environmental pollution. As a result, there is a critical need for new coating technologies which will reduce or eliminate chromate based systems yet provide adequate corrosion resistance, abrasion resistance and paint adhesion.

Table I. Common Inorganic Surface Treatments for Magnesium A	Alloy	S.
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Chemical Treatment	Type	Solution Constituents
#1	Conversion	Sodium dichromate, nitric acid
#7	Conversion	Sodium dichromate, calcium or magnesium fluoride
#17	Anodic	Ammonium bifluoride, sodium chromate, phosphoric acid
#19	Conversion	Chromic acid, calcium sulfate
#21	Conversion	Chromic acid, ferric nitrate, potassium fluoride
HAE	Anodic	Potassium hydroxide, potassium fluoride, aluminum hydroxide, sodium phosphate, potassium manganate
Iridite No. 15	Conversion	Chromic acid, chloride, nitrate solution
Bonderite 1000	Conversion	Iron phosphate

Recently, a new high performance coating for magnesium alloys has been developed which exhibits improved corrosion protection and abrasion resistance as well as providing an excellent paint base. The coating has been given the trademark, TAGNITETM, and is produced by an electrochemical process that does not employ chromates. The process and coating characteristics are described herein.

products which may be present on the alloys through the use of the mild alkaline etch. This solution, commonly used to brighten die cast alloys, shows an insignificant metal loss after a ten minute treatment. The coating process itself consists of two steps. The first step is a simple chemical process in which the magnesium alloy is immersed into a heated solution containing the fluoride ion. This solution applies a layer containing a mixture of magnesium fluoride and oxofluorides and magnesium oxide and serves as a base for the step second. The second step is an electrochemical process in which the magnesium alloy is made the anode in an electrolytic cell.

The electrolytic process is accomplished using a relatively high voltage rectifier which supplies a combination AC/DC signal to the electrochemical cell. As in other anodization processes, the magnesium alloy is the anode while the stainless coating tank serves as the cathode. The electrolytic process involves the concurrent anodization or oxidation of the metal substrate and deposition of inorganic species from the silicate containing electrolyte. As a result of the relatively high voltages, greater than 150V, a spark process develops during the deposition. The sparking action is the result of the applied voltage being greater than the dielectric breakdown voltage of the layer produced in the first chemical step and the developing coating in the electrolytic step and produces temperatures which have been estimated to be greater than 1000°C. These localized high temperatures result in the fusion of silicate and oxide species onto the metal surface. Although the heat generated from the spark is localized on the surface, the resistive heating of the solution requires a cooling system to maintain the electrolyte temperature between 10-20°C. Figure 2 is a photograph of a magnesium AZ91D panel during the deposition process with the sparks visible on the panel surface. The lifetime of these sparks is typically less than a millisecond.

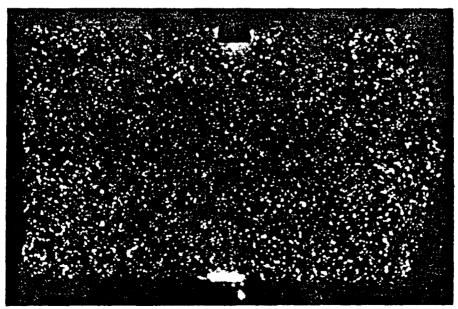


Figure 2. A photograph of a 4" x 6" test panel of magnesium alloy AZ91D during the Tagnite anodic spark deposition process.

Surface and near surface elemental analysis of the coating by ESCA indicates the

EXPERIMENTAL

Evaluation of coating performances was conducted on two magnesium alloys, AZ91D, a die cast alloy, and ZE41A, a sand cast alloy. All panels used to evaluate corrosion resistance were from the same melt so as to eliminate any variation in base corrosion rate for the bare metal due to variations in alloy composition. All coatings were applied as per specifications either in-house for the Tagnite coating or by an aerospace approved metal coating facility. In addition, all panels were entered into the salt spray chamber together to eliminate variation in chamber conditions.

Coating thicknesses were measured by an eddy current technique using an EMI International EM-2000E instrument which was calibrated with two plastic sheets of certified thickness on an alloy base of similar surface roughness as the panel tested. The arithmetic average roughness height, R_a, was measured using a Sheffield type QE profilometer amplimeter which was calibrated using a precision reference specimen. Five measurements were made across the surface of each panel using a 0.03" cut off width and 1.5" piloter stroke length. The five readings were averaged to yield the R_a value. Abrasion resistance testing were conducted using a Taber Model 5130 abraser using two C-17 abrading wheels with 1000 grams of load (ASTM D4060). The C-17 wheels were refaced before each test and after every 1000 cycles using a S-11 refacing disk. Results are reported as a Taber Wear Index (TWI) and number of cycles achieved. Corrosion performance testing was performed using a Singleton Model 20 corrosion test chamber operating as per ASTM B117. Panel evaluation was conducted as specified in ASTM D1654, method A and B. Scanning electron photomicrographs were obtained on a Hitachi S-800 scanning electron microscope.

THE COATING PROCESS

The application of the TAGNITE coating, as is the case with other coating processes, requires good cleaning practices such as those specified in MIL-M-3171.¹⁴ Typically, the cleaning procedure shown in the process flow diagram of Figure 1 is sufficient to degrease and clean the surface. In addition, this method is capable of removing minor corrosion

Figure 1. Process Flow Diagram for TAGNITE Treatment of Magnesium Alloys.

Degreaser, aqueous based 40-50°C, 1-15 min., Rinse

Alkaline Etch 70-80°C, 1-10 min., Rinse

Fluoride Pretreatment 70-95°C, 5-90 min., Rinse

> TAGNITE-8200 10-15°C, Rinse

Surface Neutralization Post-Treatment 50°C, 30-120 seconds, Rinse major constituents include magnesium, silicon, oxygen and fluorine for the coating on both the AZ91D and ZE41A alloys with a very minor quantity of potassium. For the ZE41A alloy, a minor percentage of cerium was detected, a result of the 1% rare earth composition of the alloy. The measured bonding energies indicate that the silicon atom is present in the form of silicate, not as silica, and the fluorine atom exists in its ionic form. This presence of magnesium in the coating indicates the electrolytic process involve the oxidation of the magnesium alloy substrate with the concurrent spark deposition of silicate and oxide species on the surface of the magnesium alloy. The oxidation and deposition process also results in a dimensional change for the magnesium alloy part. Cross-sections of panels which were partially masked, then coated and subsequently examined by SEM indicate that a dimensional increase of approximately 54% of the coating thickness occurs for the AZ91D alloy as compared to 46% for the ZE41A. These values are similar to those reported for the other two anodic processes. For example, chemical treatment 17 and HAE show an increase of approximately 65 to 75% and 50 to 75%, respectively. 15

The thickness of the coating can be varied from two to thirty micrometers by controlling the current density and the time of the coating process. Typically, the process is performed at a constant current density in the range of 5 to 15 A/ft² with coating times of 10 to 20 minutes for a five to ten micrometer (0.2 to 0.4 mil, type I) thickness and 45 to 75 minutes for a 20 to 25 micrometer (0.8 to 1.0 mil, type II) thickness. The final voltage, though dependent upon the current density and bath composition, typically ranges from 280 to 320 volts for a type I and 320 to 340 volts for a type II with power requirements of approximately 0.4 and 1.6 kW hr/ft², respectively.

COATING MORPHOLOGY

The coating produced during the electrochemical process yields a surface with a finite amount of porosity. The porosity is a result of the evolution of oxygen gas from the oxidation of water or hydroxide ion with the concurrent generation of sparks at the surface. Figure 3A is a scanning electron photomicrograph representing the top view of a 5 micrometer thick Tagnite coating on a AZ91D test panel at a magnification of 2000 while Figure 4A represents a 22 micrometer thick coating on a ZE41A test panel. The maximum size of the pores is typically in the range of one to five micrometers for a type I thickness and one to ten micrometers for a type II thickness with the size dependent on the electrolyte composition. concentration and the time of coating process. The increase in pore size with coating thickness may be attributed to a similar increase in spark size resulting from a greater dielectric breakdown voltage as the deposition process proceeds. Though the surface is porous, the surface texture as measured by profilometer indicates the arithmetic average roughness height (R_a) ranges from 25 to 85 microinches for coatings between 2 to 25 micrometers (0.1 to 1.0 mil) thick. The value of R_a is dependent on the time of deposition or the thickness, only marginally dependent on the current density or the rate of deposition, and is essentially independent of the substrate alloy. For example, a coating thickness of 12.5 micrometers produces a surface with a value of R, from 48 to 53 microinches for current densities between 3 and 15 A/ft².

Finally, it should be noted that although the coating has a porous microstructure,





Figure 3. Scanning electron photomicrographs: A) top view of the Tagnite coating on AZ91D (200x), B) cross-section view of the Tagnite coating on AZ91D (2000x).

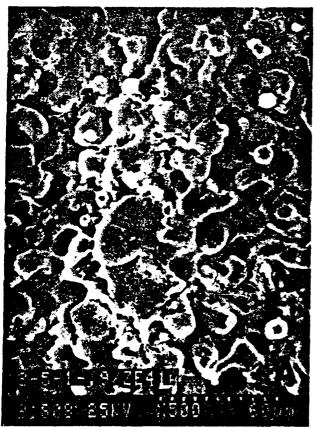




Figure 4. Scanning electron photomicrographs: A) top view of the Tagnite coating on ZE41A (500x), B) cross-section view of the Tagnite coating on ZE41A (1000x).

cross-sectional views of the coating indicate that the pores do not completely transverse the coating. Figure 3B and 4B are SEM photomicrographs of cross-sections of the TAGNITE coatings on the same alloys as shown in Figures 3A and 4A, respectively. As can be seen, the coating interface with the metal is quite good with no passageways occurring between the exterior and the base metal. Thus, the coating has the effect of preventing an aggressive environment from contacting the reactive metal substrate which would result in extensive corrosion.

CORROSION PROTECTION AND PAINT ADHESION

With the advent of high purity magnesium alloys, the corrosion rate for the base metal has been significantly reduced as compared to pure magnesium metal. In aggressive environments, however, additional corrosion protection is required and provided by the application of surface coatings. In addition, these coatings also serve as a base for painting. To test for corrosion resistance and paint adhesion, accelerated testing is performed using a salt spray chamber (ASTM B117). Table III illustrates some representative data for salt spray testing on the AZ91D and ZE41A alloys which have been treated with the Tagnite. HAE and chemical treatment 17 coatings. As can be seen, the Tagnite coating provides increased corrosion protection as compared to HAE and chemical treatment 17. For example, the Tagnite coating on AZ91D with a thickness of 5 to 10 micrometers (Type I) yields an ASTM D1654 (procedure B) rating of 8 after 28 days in salt spray while both HAE and treatment 17 are rated at 5 after just 14 days. It should be noted that the rating is based on the percentage of the total surface area that has failed due to corrosion pits, blisters or any other type of failure present. A rating of 8 represents a 2 to 3% failed area and a 5 denotes 11 to 20% of the area has failed. The best rating is a 10 which corresponds to no failures. The application of a thicker coating provides improved protection as indicated by a rating of 10 for a Type II Tagnite coating after 28 days in salt spray. The ZE41A alloy also benefits from a Tagnite coating and, as shown in table III, a type II coating typically gives a rating of 9 on panels exposed to salt spray for 14 days while treatment 17 affords only minor protection with over 75% of the area having failed (a rating of zero) after only 2 days. It should be noted that the duration of the corrosion test will be less for the ZE41A alloy than the AZ91D alloy due to the difference in corrosion rates for the base alloys.

Table III. ASTM D1654 Ratings on AZ91D Panels Subjected to Salt Spray.

Coating/Alloy	Thickness	Time	Unscribed Area (Procedure B)
Tagnite ¹ /AZ91D	Type I	28 days	8
Tagnite ¹ /AZ91D	Type II	28 days	10
Tagnite ¹ /ZE41A	Type II	14 days	9
Dow 17/AZ91D	Type I	14 days	5
Dow 17/AZ91D	Type II	14 days	5 '
Dow 17/ZE41A	Type II	2 days	· 0
HAE ² /AZ91D	Type I	14 days .	5

¹ Post-treated using sodium dihydrogen phosphate

² Post-treated using sodium dichromate and ammonium bifluoride

A comparison of the coating morphologies offers a possible explanation for the greater effectiveness of the Tagnite coating over HAE and treatment 17 towards corrosion. Cross-sections and surface examination of the coatings by SEM indicate the pores in the Tagnite coating are smaller and more uniform in size and distribution as compared to the other two anodic processes. Further, the Tagnite coating shows considerably fewer interconnecting pores which completely transverse the coating to the base metal substrate. In contrast, the coating from treatment 17 typically produces the deepest pores with a high degree of interconnectivity. As a result, the Tagnite coating effectively isolates the magnesium metal substrate from the corrosive environment.

The corrosion resistance of the magnesium alloys may be further improved by sealing the coatings with paints. In this case, test panels of the AZ91D alloy which were coated with 10 to 25 micrometers of the Tagnite coating were primed with a melamine polyester primer and then painted with a thermosetting acrylic enamel top coat. The panels after being scribed were placed into salt spray for 28 days, with an evaluation of each leg of the scribe being performed every seven days. The data, shown in Table IV, indicate consistently high ratings with no corrosion migration under the scribe or corrosion in the unscribed areas. The lack of corrosion creepage from scribe is indicative of the good paint adhesion characteristics of the coating and may be attributed to its surface morphology.

Table IV. ASTM D1654 Ratings on AZ91D Panels with Tagnite, Painted and Scribed.¹

	Scribed Area (Procedure A))	Unscribed Area (Procedure B)	
Sample No.	7 day	14 day	21 day	28 day	28 day
10-22-3	10	10	10	10	10
10-23-3	10	10	10	10	10
10-24-1	9	10	10	10	10
10-25-2	9	10	10	10	10
10-29-6	10	10	10	10	9

¹ Testing (ASTM) and evaluation (ASTM D1654) was carried out by R.W. Murray, The Dow Chemical Company, Technical Service and Development, Lake Jackson Center, Texas.

The effect of primer and top coat on the corrosion resistance and paint adhesion was also examined on the ZE41A alloy. When panels of this alloy, treated with the Tagnite and treatment 17 coatings, are painted with one coat of primer (MIL-M-23377E) and subjected to salt spray for 28 days, extensive corrosion occurs for the treatment 17 coated panels with typical ratings of 3 (procedure B). In contrast, the Tagnite coated panels are rated as 10 (procedure B). Additionally, panels were also coated with the Tagnite and treatment 17 coatings, painted with one coat of primer (MIL-M-23377E) and a top coat (MIL-C-46168D). In this case, the paint adhesion characteristics were tested by scribing the panels before placing them together in salt spray for 28 days. Due to the higher corrosion rate of this alloy, corrosion pits develop on the scribe for both coating systems; however, the extent of corrosion migration under the scribe or the degree of paint adhesion to the anodic coatings is considerably better with the Tagnite coating than with treatment 17. Ratings (procedure A) of 5A and 9A (with a single low value of 7A) are typically obtained for treatment 17 and Tagnite coatings, respectively.

ABRASION RESISTANCE

Abrasion resistance has been determined on Tagnite, treatment 17 and HAE coatings on AZ91D as well as the Tagnite coating on ZE41A. Table V illustrates representative data in the form of the number of cycles and a Taber Wear Index (TWI). As can been seen from the data, the Tagnite coating on both AZ91D and ZE41A is considerably more wear resistant than either HAE or treatment 17. Though the abrasion resistance will largely be dependent

Table V. Abrasion Test Results.				
Sample	TWI	Cycle	Comments	
AZ91D, TAGNITE, 0.3 mil	9	5000	< 10% metal exposed	
AZ91D, TAGNITE, 0.6 mil	8	7000	< 10% metal exposed	
AZ91D, TAGNITE, 0.8 mil	7	5000	< 10% metal exposed	
AZ91D, TAGNITE, 0.9 mil	6	6000	< 10% metal exposed	
AZ91D, HAE, Type I (0.2 mil)	142	75	10% metal exposed, coating gone after 200 cycles	
AZ91D, HAE, Type II (2.6 mil)	142	1800	10% metal exposed; coating gone after 3000 cycles	
ZE41A, TAGNITE, 0.2 mil	6	1000	10% metal exposed	
ZE41A, TAGNITE, 0.5 mil	7	5000	10% metal exposed	
ZE41A, TAGNITE, 0.6 mil	14	5000	10% metal exposed	
ZE41A, TAGNITE, 0.8 mil	12	7000	10% metal exposed	
ZE41A, TAGNTTE, 1.0 mil	14	9000	10% metal exposed	
AZ91D, TAGNITE, 0.5 mil	14	3000	bare metal starting to show ²	
AZ91D, Treatment 17, 1.0 mil	37	1000	coating gone after 500 cycles ²	
AZ91D, HAE, 1.0 mil	104	1000	coating gone after 500 cycles ²	

¹ Taber Wear Index (TWI) defined as TWI=(A-B)x1000/C where A is the weight of the test specimen before abrasion in milligrams, B is the weight of the test specimen after abrasion in milligram and C is the number of cycles of abrasion recorded.

upon the chemical nature of the coating, the significant increase in resistance may be partially attributed to the coating process in which the localized high temperature, occurring during the spark deposition, fuses the silicate and oxide species onto the metal substrate surface.

ENVIRONMENT

Over the last several years, concern has been raised regarding the impact the metal finishing industry has on the environment. When one considers that the commonly used materials include chromium, cadmium, zinc, lead, copper, nickel, cyanides and VOCs, it is not surprising that the EPA has listed the metal finishing industry as a major contributor to environment pollution.¹³ Due to the demanding environment in which their products function, the aerospace industry has become a major user of metal finishing systems, and have recently expressed concerns regarding VOC emissions, utilization of 1,1,1-trichloroethane, hexavalent chromium emissions, the land ban and hazardous waste disposal costs, OSHA

² Data provided by R.W. Murray, The Dow Chemical Company, Lake Jackson Research Center, Freeport, Texas.

compliance and source reduction and recycling. As a result of the increasing inevitable government regulation of hazardous wastes, the industry will be required to become more environmentally responsible through the implementation of waste minimization programs and/or the utilization of less hazardous materials.

Chromates are one of the principal chemicals used in metal finishing industry, particularly those dealing with magnesium based alloys. The chromate ion is an excellent corrosion inhibitor. It is used as a paint pigment, employed in chromate conversion coatings, as well as in anodizing baths for aluminum based and magnesium based alloys and as a post-treatment for sealing anodized surfaces. However, chromates are known to be highly toxic and carcinogenic. The oral ingestion of 1-2 grams of chromic acid or 6-8 grams of potassium dichromate is reported to cause kidney failure, liver damage, blood disorders and even death. In addition, exposure of chromates to the skin for prolong periods may cause rashes, blisters and ulcers while inhalation may cause lung cancer. Due to these health risks, OSHA limits insoluble chromates in the air space to 1mg/m³ per 8 hour day per 40 hour week and has specified that chromate containing paints must be labelled with a lung cancer warning. Is

There are several approaches to the chromium issue. One option is to improve the handling procedures in the work place so as to comply with the allowable chromate exposure limits. Since it is likely that the regulations will only become more restrictive, this alternative will serve only as a temporary basis. Another alternative is to reduce or eliminate chromate containing waste by the application of new technologies. For example, a study by VanCleave¹⁹ has resulted in a significant chromium reduction in which chemical treatment 21 was found to be a suitable replacement for treatment 1, both chromate containing solutions, thus permitting the elimination of a planned 7600 gallon treatment 1 tank in their new finishing facility.

Though the implementation of chromium reduction programs is clearly needed, the best alternative is the utilization of chromium free materials. Recently, Hinton^{20, 21} has presented several alternatives to chromate conversion coatings and paint pigments for aluminum based alloys. For magnesium alloy users the elimination of chromate may be more difficult, partly due to the greater chemical reactivity of magnesium. Many of the commonly employed conversion coatings are chromate based (see Table I) while the common cleaning solution for removing corrosion products and old finishes is chromic acid. Further, current specifications such as MIL-M-3171 require the application of chemical treatment 1 to sand cast magnesium alloys for corrosion protection during shipment and storage.

As discussed earlier chemical treatment 17 and HAE are routinely applied to magnesium alloys when increased corrosion protection is required. Treatment 17 contains approximately 8% by weight sodium dichromate and, although it is reported that the solution is only infrequently disposed, thus generating only small volumes of chromium containing waste water through dragout, the presence of large processing tanks still results in employee exposure and the potential for environmental damage should a spill occur. In addition, even though disposal is infrequent, chromium is introduced directly into the environment from the coating itself. Based on the operational parameters for treatment 17 approximately 0.1 to 0.2

oz of chromium would be introduced into the environment per square foot of metal coated.²² Although HAE is not a chromate containing solution, the coating requires a post-treatment in ammonium bifluoride and sodium dichromate for all grades except grade 1¹⁵ and thus utilizes chromium compounds in the overall process.

A significant chromate reduction may be made by first replacing chromate conversion coatings which are used for temporary protection with oil. It has been reported that magnesium components may be stored from 1 to 5 years if the alloy is oiled and sealed in a polythene bag containing a desiccant.²³ Furthermore, the use of oil instead of the conversion coatings will allow the metal surface to be cleaned using alkaline cleaners without relying on chromic acid. Finally, the application of a chromium free coating system such as the Tagnite coating will eliminate chromates in the anodizing and/or post-treatment baths.

CONCLUSIONS

Reduction and elimination of chromium based systems will be a major endeavor in the metal finishing industry as the governmental regulation of chromium becomes more and more restrictive. For magnesium based alloys chromium reduction may be achieved by replacing the conversion coating used for temporary storage with oil and by the application of chromium free coating systems such as Tagnite. The Tagnite system provides greater corrosion protection, enhanced paint adhesion and better abrasion resistance than either chemical treatment 17 or HAE.

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Inorganic Chemistry as an Option for Formulating High Solids, Low and Zero - VOC Architectural and Industrial Maintenance Coatings

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INTRODUCTION

Architectural and Industrial Maintenance (AIM) Coatings are required to protect a wide range of substrates from degradation by a very wide range of environments. Coating systems presently used rely almost entirely on organic polymers. These chemistries are well established and give proven protection to stationary structures in many environments. Inorganic polymers have also been used in the form of inorganic zincs coatings, but these products have limitations in that they are used only on ferrous substrates, have poor aesthetic properties, are not very compatible with organic topcoats and do not give performance in acidic and caustic immersion service. However, their performance in these limited applications exceed their organic counterparts. Further, the performance properties of silicone and silicate resin in baked coatings is well documented and they provide superior properties in heat, UV and chemical resistance. Silicone resins have also been used to improve the performance of organic polymer coatings. They can improve such characteristics as heat and sunlight UV resistance. Until recently, with the exception of inorganic zincs and some organic/inorganic copolymers, inorganic polymers were not feasible for stationary structures because they required baking. A breakthrough in curing technologies has led to polymers that will film form under ambient conditions to give inorganic backbones. Further, these coatings can be formulated to very low VOC's either in solvent, 100% solids or water based options. The performance of these products, in general, exceeds those of organic based coatings.

DISCUSSION

Terminology

For clarity, Table 1 gives definitions of the chemical terminology used in the following discussion. In coating compositions, the typical resins using the silicon-oxygen bond as the repeating unit in the backbone are silicones and silicates. The term polysiloxane can include silicones, but it is used herein in its broadest sense, that is, any polymeric structure that contains repeating silicon-oxygen groups in the backbone, side chains, segments or cross links regardless of substitution on the silicon atom. The presence of certain organic groups bonded to the silicon atom in silicones and polysiloxanes moderates physical, mechanical and chemical properties, typically in an advantageous fashion. Oxysilane refers to a silicon based structure in which the silicon is bonded to up to four alkoxide or hydroxyl groups thereby rendering that structure reactive to certain condensation reactions; the oxysilane may be monomeric, polymeric or a pendant group of a larger molecule.

Comparison of Inorganic and Organic Binders

To understand the performance difference of organic and inorganic products, we must first comment on comparative chemical properties of the binders (See Table 2). The high bond strength of the Si-O bond compared to a typical C-C bond gives the inorganic structure strength making them more durable in comparison to carbon based structures. Further, this structure is more inherently heat stable leading to heat resistance up to 2000°F. By comparison, epoxies and polyurethanes are limited to the 200-300°F.

range. Inorganic silicone-oxygen bonds are unaffected by sunlight and ultraviolet attack. By comparison, organic binders such as epoxies and alkyds typically show early chalking and fading and polyurethanes and acrylics will show fading and gloss loss in a 3-5 year period. Since Si-O is already oxidized, polymers based on such a backbone are not affected by atmosphere oxygen and most oxidizing chemicals. In contrast, organic polymers will eventually oxidize and degrade. An inorganic structure is not combustible, organic polymers will burn and generate smoke and toxic furnes.

Inorganic Binder Chemistry

Traditional silicone and oxysilane curing involves a process called hydrolytic polycondensation in which an alkoxide silane is first hydrolyzed and the resulting silanols are condensed to a polymer network (See Figure 1). The innovations being described involve catalysis of this process or direct condensation and the selection of appropriate silicone and oxysilane precursors to produce binders of use in AIM coatings (See Table 3).

Coating Formulation: Silicones

Silicone copolymers (containing either alkyd, acrylic or polyester coresins) are well known. The amount of silicone resin incorporated in the copolymer determines the properties of the coating. The binders are manufactured by condensation at high temperatures. The AIM coatings curing and drying properties are dominated by those properties of the organic component. Their solids and VOC content are also dominated by the organic component?

Coating Formulation: Polysiloxane

The chemistry described above has been successfully applied to create pure polysiloxane network binders. These binders have been formulated into pure polysiloxane AIM coatings having maximized thermal, chemical and UV resistance. Further, polysiloxane/organic "hybrids" AIM coatings have been formulated that significantly enhance the properties of the selected traditional organic resin based coating. As well as high performance properties, these formulations offer advantages in VOC content. This chemistry increases molecular weight of the binder during the curing of the film to produce solid polymer networks. The silicone and oxysilane precursors used are selected not only for performance but for their very low viscosity allowing for low VOC content formulations. Pure solvent based polysiloxane formulas have been produced with volume solids contents of 80-95%. These precursors in hybrid systems are also selected for their compatibility and diluting effect on the organic components giving coatings a volume solids content of 80-100%. Water borne inorganic binders have also been formulated into coatings. The pure inorganic versions use silane and silicates as precursors and these systems require no cosolvents and have 0 VOC. Water borne organic hybrids can also be formulated at low VOC, however, these do require some cosolvent to form a film with acceptable performance.

EXAMPLES

The following examples are offered to demonstrate the unique properties provided by utilization of polysiloxane chemistry in AIM coatings.

Polysiloxane Topcoats

Topcoats have been formulated with both pure polysiloxane and polysiloxane/organic hybrid binders. Table 4 describes the formulations that exploit the ultraviolet resistance of the siloxane bond. These formulas have similar appearance to polyurethanes. Table 5 outlines the formulas' characteristics. The UV resistance of both these formulas has proved during accelerated weathering tests to be more resistant than traditional organic based topcoats (See Figure 2). Another interesting property of these polysiloxane coatings is their inherent compatibility with inorganic zinc silicate (IOZ) primers. As dis-

cussed previously, IOZ primers have superior corrosion performance properties, but limited compatibility with organic topcoats. Traditionally, a 3 coat system utilizing an IOZ primer has been used as a high performance system in the protection of steel in aggressive industrial atmospheres (See Table 6). The epoxy midcoat is used to tie the IOZ primer to weatherable topcoats that cannot be applied directly to this primer. The compatibility of the polysiloxane topcoats with the IOZ primers allows a 2 coat system with obvious advantages (See Table 7).

Water Based System

The above system describes solvent borne topcoats. An alternative to the 2 coat system above is a 0 VOC water based system. IOZ primers are available for both systems that contain 0 VOC. This technology has been used to formulate a 0 VOC pure polysiloxane, water based topcoat. As with the previous system, the topcoat is very compatible with the IOZ primer. This system will provide corrosion protection equivalent to the organic and solvent based polysiloxane system. The finish of this topcoat is flat and so is not usable where a gloss finish is requested. However, this product will maintain its finish and not chalk or discolor much longer than organic finishes. Table 8 shows the coating characteristics of this product.

Heat resistant Polysiloxane Coating

Compositions that contain pure polysiloxane binder networks have been formulated that provide maximum heat and/or chemical resistance. Heat resistance in excess of 1100°C (2000°F) can be achieved. Typical formulations will contain micaceous iron oxide (MiOx) as the major filler component; the most successful formulations have the binder to filler ratio as near as possible to the CPVC. Table 9 gives a description of this type of formulation, Figure 3 shows thermogravimetric analysis for this type of formulation and Table 10 gives the coatings' characteristics. The weight loss over the temperature range is around 10%; this accounts for the loss of the organic substituent groups, absorbed water and residual solvent. The remaining film maintains mechanical integrity and continues functioning as a barrier coat even after high temperature exposure. Table 11 is a summary of representative properties of this type of formulation*. Typical applications would include stacks, the exterior of reactors and on piping under insulation. There are no equivalent organic coatings with this level of performance. The closest heat resistant ambient cure products are silicone alkyds. Their temperature resistance can be as high as 1000°F but their VOC content is generally above 400 grams/liter.

Chemically Resistant Polysiloxane Coating

The same binder system can be used with an optimized pigment package to achieve chemical resistance of a scope not given by organic systems (See Table 11). Indeed, because this type of formulation is essentially inorganic, it behaves like a zinc silicate without the acid exposure and chemical reactivity limitations. Table 12 describes the coatings characteristics. Polysiloxane tanklining prototypes are resistant to virtually all solvents, organic acids and mineral acids in certain concentration ranges. However, pure polysiloxanes are not resistant to alkali. Table 13 is a summary of the representative chemical resistance of this type of formulation. Tank linings based on organic binders are available. Ambient temperature cured organic systems generally have good alkali resistance, but only moderate to poor resistance to solvents and acids. These products are available in low VOC content formulations, however, to approach the resistance of the polysiloxane to solvents and acids, force cure of bake systems are necessary. These systems are generally higher in VOC content and often include aromatic amine hardners that present toxicity problems during application.

In ongoing formulation work, epoxy/polysiloxane hybrids have been developed that cure at room temperature and combine the resistance of polysiloxane to acids and solvents with epoxies resistance to alkali. These coatings have shown the best combination of chemical resistance.

CONCLUSIONS

In summary, it should be emphasized that a new formulation chemistry has been described. The products used as examples typify the first generation of oxysilane and polysiloxane based systems. This chemistry offers the opportunity for quantum improvements in such performance areas as heat.chemistry allows the retention of desirable properties in existing systems while enhancing those areas needing improvement. The use of this chemistry is consistent with the need for developing high-performance-AIM coating systems that offer reduced environmental, health and safety hazards.

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TABLE 1 Terminology

Silicon

The element (Si)

Silane

Substituted silicon compounds

Oxysilane

Silicon compounds with at least one substituent an alkoxide, hydroxide or aryloxide

Silicate

Metal salt of silicon-oxygen anion

Silica

Sand; silicon-oxygen compound

Siloxane

Compounds with 2 or 4 oxygens bonded to silicon

Polysiloxane

Polymer with silicon-oxygen backbone

Silicone

Polysiloxane with organic substituents on each silicon, typically 2

Organic

Carbon based compounds; polymers with carbon-carbon units with backbone

TABLE 2 Comparative Properties Inorganic and Organic Binders

- Binder Backbone
 /
 C C 83 Kcal/mole
 /
 Si O 108 Kcal/mole
- 2. Si-O is UV resistant
- 3. Si-O is already oxidized
- 4. Si-O is not combustible

TABLE 3 Advances in Siloxane Coating Chemistry

- * Low/Ambient Temperature Curing
- * Silicone Intermediates
- * Oxysilane Prepolymers
- * Formulation Technique
- * Inorganic/Organic "Hybrids"

TABLE 4 Pure Polysiloxane Coating Topcoat Formula

Description

Binder Pure Polysiloxane Backbone
Silicon Substituents Selected/Balanced for UV Resistance and Film Properties
Cross Link Density Balanced for Film Properties
 Pigment Selected for Appearance
Full Gloss Range
High, Semi, Flat
 Curing Ambient Conditions
Single Package
Catalyzed Hydrolytic Polycondensation

Hybrid Polysiloxane Coating Topcoat Formula

Description

1.	Binder	Mixed Polysiloxane - Acrylic Backbone Silicon Substituents Selected/Balanced for UV Resistance and Film Properties Acrylic Selected for Appearance, Physical, Mechanical Properties Cross Link Density Balanced for Film Properties
2.	Pigment	Selected for Appearance Full Gloss Range
		Full, Semi, Flat
3.	Curing	Ambient Conditions
		Catalyzed Polycondensation

TABLE 5

Characteristic	Pure Polysiloxane Topcoat	Hybrid Polysiloxane Topcoat	
Number of Components	1	1	
Volume Solids, %	86	85	
VOC, grams/liter	129	122	
Dry to Touch, hrs at 70°F	2	2	
Dry Through, hrs at 70°F	6	8	
Application	Spray, Brush and Roller	Spray, Brush and Roller	

TABLE 6

A. Inorganic Zinc Silicate Primer	Epoxy Midcoat	Polyurethane Topcoat
Corrosion Control	Adhesion Promoter; Tie coat	Appearance Weatherability

- Three coats required to make the organic coatings, notably polyurethane, compatible with IOZ
- B. Inorganic Zinc
 Silicate Primer

 Corrosion Control

 Barrier
 Appearance
 Weatherability
- * Two coats because polysiloxane is inherently compatible with IOZ
- * No need for epoxy midcoat to make system compatible
- Epoxy film not needed for corrosion control; IOZ is sufficient

TABLE 7 IOZ/Polysiloxane System Advantages

Better weatherability

Same corrosion resistance as three coat

Less manufacturing touch-up/repair

Faster manufacturing turn-around

Lower VOC emissions

Reduced waste generation/disposal

Components

TABLE 8 Coating Characteristics of Pure Polysiloxane Water Based Topcoat

1

_ •	
Volume Solids, %	43
VOC, grams/liter	0
Dry to Touch, hrs at 70°F	0.25
Dry Through, hrs at 70°F	12
Application	Spray

TABLE 9 Polysiloxane Coatings Heat and Chemically Resistant Example

Description

1.	Binder	Pure Polysiloxane Background
		Phenyl and Mathyl Substituents to Balance Properties
		Oxysilane Cross Linking to Maximize Heat and Chemical Resistance
2.	Pigment	Micaceous from Oxice
	_	Level to Maximize Heat Resistance
		or
		Silica/filler Blend to Maximize Chemical Reistance
3.	Curing	Ambient Conditions
		No Baking
		Hydrolytic Polycondensation

TABLE 10 Coating Characteristics for Heat Resistant Polysiloxane

Characteristic	
Components	2
Volume Solids, %	90
VOC, grams/liter	96
Pot Life, hrs	6
Dry to Touch, hrs at 70°F	1
Dry Through, hrs at 70°F	24
Application	Spray

TABLE 11 Polysiloxane Coatings Heat Resistant Formula

1.	Salt Spray	
	5000 Hrs	
	Blistering (ASTM D714)	10
	Corrosion (ASTM D1654)	9
	Scribe (ASTM D1654)	10
	Adhesion	Excellent
2.	Heat Resistance	
	TGA - Total Weight Loss, to 1000°C	
	10%	
	Torch - 1510°C, Discoloration	
3.	Condensing Humidity	
	4500+ Hrs	
	Blistering	10
	Corrosion	9
	Adhesion	Excellent
4.	Atlas Cell (Salt and Deionized Water)	
	1000 Hrs	
	Vapor Phase	Pass, No Blisters
	Liquid Phase	Pass, No Blisters
5 .	Chemical Resistance (Representative)	
	Immersion at 25°C, (Test time, hrs.)	
	Acetic Acid	(4000)
	50% Sulfuric Acid	(4000)
	19% Hydrochloric Acid	(3000+)
	Acetone	(8000)
	Mathylene Chloride	(8700)
	JP -4	(1200+)
	Xylene	(8700)

TABLE 12 Coating Characteristics for Chemically Resistant Polysiloxane

Characteristic	
Components	2
Volume Solids, %	80
VOC, grams/liter	9 9
Pot Life, hrs	6
Dry to Touch, hrs at 70°F	1
Dry Through, hrs at 70°F	24
Application	Spray

TABLE 13 Polysiloxane Coating Immersion Formula Representative Chemical Resistance

Acetone

Ketones

Methanol

Alcohols

Xylene

Aromatics

Methylene Chloride

Chlorinated Hydrocarbons

Fatty Acids

Acetic Acids

Organic Acids

Triethanol Amine

50% Sulfuric Acid

83% Phosphoric Acid

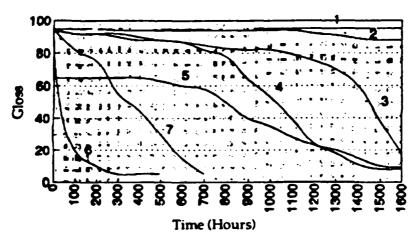
10% Nitric Acid

10% Hydrochloric Acid

Not Resistant to Alkali

Figure 1.

Hydrolytic Polycondensation of Oxysilane



¹ Polysiloxane	² Acrylic Polysiloxane	³ Acrylic Polyurethane
⁴ Silicone Alkyd	⁵ SG Acrylic Latex	Z Alkyd
6 Epoxy		·

Figure 2. Comparison of the accelerated ultraviolet resistance (QUV) of various generic classes of coatings

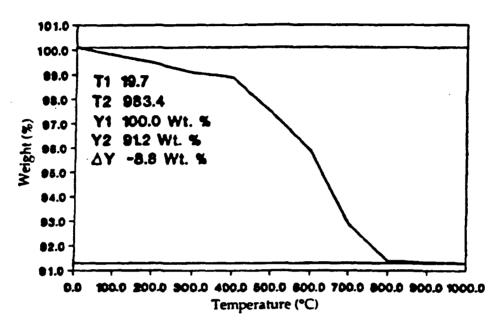


Figure 3. Thermogravimetric analysis of heat resistant Polysiloxane

SESSION 7

HIGH SOLIDS AND WATER-BASED COATINGS

PAPERS PRESENTED:

"The Development of Practical Zero-VOC Decorative Paints"

by

Richard Tuckerman

David W. Maurer

The Glidden Company

Cleveland, Ohio

"New Environmentally Acceptable Metal Coating Systems"

by

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and

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"Water-Reducible Polyurethane Coatings for Aerospace Applications"

by

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THE DEVELOPMENT OF PRACTICAL ZERO VOC DECORATIVE PAINTS

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The objective of this paper is to paint a picture of some of the technical challenges associated with the development of a zero VOC decorative paint. The development of practical, zero VOC decorative paints presented The Glidden Company with a unique opportunity to combine the resources of many groups toward a common goal. These included our internal technical teams working with external supplier technical groups; Glidden's corporate marketing, manufacturing, and product regulatory and safety teams; as well as the regulatory and environmental communities as a whole.

The paint industry has been in the legislative and environmental spotlight for several decades now; Even a brief review of the regulatory climate would include the following legislation:

The Clean Air Act
The Clean Water Act (CWA)
The Toxic Substance Control Act (TSCA)
The Resource Conservation and Recovery Act (RCRA)
The Emergency Planning and Community Right to Know Act (RCRA)
Solid Waste Disposal Regulations
State Implementation Plans (SIP)
State VOC Regulations
"Regulatory-Negotiation" Process (Reg/Neg)

The paint industry, as a whole, has been extremely responsive and responsible in relation to these requirements. Often, and more importantly, the paint industry has been proactive over an even longer time frame in introducing products that are better, safer, and more convenient for the end user. The introduction of latex paints, electrocoats, powder coatings and waterborne can liners are just a few examples.

The trend towards waterborne paints over the past three or four decades has lead to the present split of 75% waterborne, 25% solventborne in the decorative paints market. In some segments of the decorative paints market, ie. wall paints, the percentage for waterborne paints is even higher, at least 90%.

A typical solventborne decorative coating contains about 45% solvent, while its latex counterpart contains approximately 7%. However, when weighted by the proportion of total decorative products made up of waterborne paints (at least 75%), we see that the contribution of solvents by waterborne paints is still significant. We estimate that 20% of VOC emissions from decorative paints are given off by conventional latex paints.

It was from this perspective that The Glidden Company viewed the opportunities afforded by a joint project with a major latex supplier as an opportunity to take action on a significant contributor to VOC's. This would be a first step, placing Glidden firmly in the lead in the inevitable drive to remove petroleum based solvents from decorative paints.

The initial challenges of this project did not deal with technical issues, but with conceptual ones - the fundamental goals and definitions which describe both the project and the product. Working together, Glidden's technical, marketing, product safety group, along with the latex supplier developed a primary goal that met the recognized needs for real accomplishment and commercial success in the marketplace.

Our stated project goal was "to develop a practical, commercially viable zero VOC decorative paint with all of the positive attributes of current solvent containing latex paints."

The resultant product target became a high quality latex semi-gloss wall and trim paint with wet adhesion, block resistance and durability. We believed that these specific qualities were essential elements and would present the most rigorous challenge in formulating without solvents.

To insure a true "break through" technology, the Glidden team also established rigorous criteria for solvent elimination. Not only must the product be free of functional solvents, containing none of the coalescing aids or glycols used in current latex paint technology, but it must contain no incidental solvents which could be carried into the end product (usually in small amounts) via other paint components.

The technical challenge could now be clearly established from the goals and definitions reviewed above. To summarize this challenge the target product a high quality latex semi-gloss, must contain no solvents, incidental or functional, and must have applied characteristics - e.g. film build and open time, flow and leveling, low temperature film formation, adhesion to hard glossy surfaces, "block resistance," scrubbability and final appearance of high quality products based on standard latex technology.

The following is a discussion of paint properties directly affected by the two major types of functional solvents - coalescents and glycols.

In standard latex paints, a relatively hard polymer is used to impart film toughness, durability and lack of thermal tack to the applied paint film. This polymer, however, may form only a marginally performing film at normal application temperatures (75 degrees F) and none at all at lower temperatures (40 to 60 degrees F). A coalescing solvent, which can partially solvate or soften the outer portion of the discreet latex particles, is added so that when those particles come into intimate contact during the drying of the paint film they will deform and

coalesce, forming a continuous film. These solvents leave the film during the drying process, thereby imparting no permanent softening to the film.

Glycols, such as ethylene glycol and propylene glycol are added to latex paints to modify the free liquid phase. Their primary function is to moderate the rate of dry of a paint film and thereby impart several useful properties to the paint. These properties are better application through increased open or working time, better flow and leveling (both through slowed evaporation and modification of surface tension), and improved gloss. They can also decrease a paint's susceptibility to freeze/thaw instability during Winter transport and storage.

The key to formulation without these components begins with the use of a novel latex that can form a film at low temperatures without solvents yet can be hard enough to promote toughness and prevent thermal tack. Having established that the neat latex could form a film at low temperatures without the use of solvents, an initial paint could be made.

The positive properties of this initial paint formulation mirrored closely many of the performance characteristics outlined above. It exhibited low temperature film formation, acceptable gloss, acceptable open time, adhesion, block resistance, and durability (scrub). This was not an unexpected result, as these properties are dependant in large measure on the quality of the latex designed.

The goal, however, was to produce a practical semi-gloss wall and trim enamel and several properties were still substandard. Chief among these were flow and leveling and application characteristics, specifically film build (thickness) and feel under the paint roller.

Beyond these "superficial" but critical attributes were a host of other paint properties, hopefully taken for granted by the end user, but of major importance to the paint formulator. These include in-can stability (viscosity changes), control of syneresis (separation in-can), opacity efficiency (TIO, utilization), foam control, and in-can resistance to bacteriological contamination. Each of these additional properties were judged to be marginal or deficient in the initial paint, and it was here that the technical challenge was most tested against the zero VOC definition established for the project.

The properties mentioned above are controlled by the coatings formulator through the use of additives. These additives make-up approximately 5% of the final liquid paint. It is an understatement to say that the formulation of modern, practical waterborne paints would be impossible without these materials.

Paint additives which are of primary interest in this discussion are: rheology control agents including thickeners and

thixotropes, defoamers, dispersants, surfactants, and in-can preservatives. This list matches-up well with the list of deficiencies noted in the initial solvent free paint formulation.

In many instances these additives, common to all latex paints, contain solvents themselves. These are either carriers for the active components, part of the active mixture, or merely residual components from the product synthesis. The key formulating challenge was to identify specific additives that were both effective and solvent free. This work was a cooperative effort with raw material suppliers, who helped identify or make zero VOC additives and the Glidden technical teams use of several experimental design techniques, including full & fractional factorial designs, titration/concentration studies, and three & four component mixture response surface designs.

In concluding this section covering the challenges faced in the development of the initial solvent free paint, we can cite a specific unexpected consequence of formulating latex products with no solvent components. During the development work from an initial paint to the final prototype, the formulating team discovered a large number of samples that exhibited microcracking This microcracking was followed and observed upon drying. throughout the drying process. It began as discreet, pinpoint discontinuities in the wet film that gradually expanded and often interconnected, forming the final cracks. This manifestation of destabilization was evaluated in dozens of samples before a root cause was found. It was apparent that the removal of all solvents and solvent containing components from the free liquid phase of the paint has a profound effect on the paint's ability to accommodate hydrophobic components. This lack of "bridging" solvents" in the free liquid phase influences stability properties from short-term storage through to the final application and dry of the paint film.

The final prototype and its matte sheen companion was rigorously tested with consumers in "blind trials" comparing the solvent free paints with their conventional latex counterparts. Consumers showed a significant preference for the solvent free paints. An "eggshell" sheen version was created and tested with professional painters. This product branded, "Lifemaster 2000", has been aimed at the institutional market - hospitals, schools, etc...

Beyond achieving the performance milestones which would assure users of no compromises, these new Glidden products "Spred 2000 and Lifemaster 2000" bring environmental benefits leading the way for the decorative paints industry. The absence of solvent emissions is the technical underpinning for major reductions in paint odor. Of course, no VOC's are released which can react with nitrogen oxides in the presence of sunlight to contribute to urban smog.

These environmental benefits have been recognized by a variety of organizations including regulatory, scientific

testing, and environmental groups. Examples include the South Coast Air Quality Management District 1992 "Clean Air Award", certification of Spred 2000 as containing "No Smog Producing Chemicals" by Scientific Certification Systems (Green Cross), and the National Audubon Society who used Lifemaster 2000 in their new headquarters building in New York City - a showcase for environmentally conscious architecture.

In conclusion, The Glidden Company would like to emphasize that the development of a practical zero VOC decorative paint, although a technical challenge, was more importantly a multidisciplinary challenge requiring innovations of our technical, marketing, manufacturing and product safety groups, as well as outside suppliers, coatings specifiers, and end users. It is the recognition of those challenges and the ability to marshall an organizations resources to create a viable solution, which is the ultimate and lasting benefit.

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

NEW ENVIRONMENTALLY ACCEPTABLE METAL COATING SYSTEMS

By:

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NEW ENVIRONMENTALLY ACCEPTABLE METAL COATING SYSTEMS

In this paper we are describing a range of decorative and protective polyurethane coating processes for metals which can replace decorative electroplating, anodizing, painting and in some cases powder coating. Conventional plating, anodizing and painting processes all produce environmentally unacceptable effluents which contaminate local air, water, or both. Although such effluents can be treated in order to minimise the impact on the environment, new regulations are making treatment costs prohibitive and even when compliance is achieved there is usually some form of waste to dispose of.

Our processes marketed under the name of Clearclad and Anoclad are relatively new to the USA. Marketing only began here about 12 months ago. In spite of this they are already well tried and proven processes. There are now well over 300 production lines operating throughout the world. A number have now been in production for over 7 years.

The processes are based on the technology known as Electrophoresis. This process has been known for well over one hundred years. The first extensive use of the process was in the 1960's when an anodic coating method for priming car bodies was developed by Brewer and the Ford Motor Company. All the early processes were Anodic. This is because the chemistry available at the time favoured the production of resins suitable for the electrophoretic deposition onto parts forming the anode in the electrical process. The problem with anodic processes is that, except in the case of aluminium or very inert metals, making the part to be coated anodic in an electrolyte causes dissolution and attack of the metal resulting in discolouration of the applied coating.. This may be acceptable for undercoats, but is completely unsatisfactory for one coat decorative systems. These systems only became practicable with the development of cathodic electrophoretic systems within the last 12 years. The new cathodic materials are based on polyurethanes and will give clear or opaque coatings on any metal in a variety of colours and effects. They are quite hard at 3-5H pencil hardness, wear resistant and have excellent exterior durability.

THE PROCESS

Electrophoresis is the process which occurs when two electrodes are immersed in a colloidal solution and a voltage is applied across them. Current flows and one of the electrodes becomes coated with a layer of the material in the disperse phase. The electrode coated can be either the cathode or the anode depending on the charge on the dispersed particles. Whilst the process is driven by the applied voltage, transport and discharge of the dispersed particles is largely influenced by other processes. Transport of particles is mainly by thermal and mechanical agitation and the maintenance of a sufficient concentration of the disperse phase in the colloidal solution. Discharge and coating formation are strongly influenced by discharge of ions around the electrode, causing a pH change which destabilizes the emulsion. The disperse phase particles around the electrode lose their charge, coagulate and stick to the surface of the electrode. At the same time, the continuous phase material trapped in the layer is squeezed out by electro-osmosis. The result is a quite "dry" electrically insulating layer forming on the electrode. Once the easily accessible areas are coated, the high resistance of the coating

causes the current to be diverted to uncoated areas until the entire surface of the electrode is covered. There are, however, limits to this process. The two processes of electrophoresis and electrolysis are, in some respects, competing. For this reason, the continuous phase (water in most cases) must have quite a high resistance or all of the applied voltage will go to drive electrolysis instead of electrophoresis. This in practice means that the water, which is the continuous phase, must be of high purity and relatively free from dissolved ions. Because of the high resistance of the disperse phase, the applied voltage can only drive the deposition current over a limited distance. This can be increased by increasing the voltage, but again there is a limitation. Any coating can only resist a limited voltage. Once this is exceeded, the coating breaks down, the current increases, the increased local current causes local heating of the solution and coating causing film rupture. Electrophoretic coating materials are carefully formulated to give maximum throwing power, but this must be consistent with the wet coating having sufficient conductivity to enable the required film thickness to be built up. The current state of the art enables thickness of 25 to 40 microns to be coated, whilst giving very good throwing and covering power; much better than can be achieved with electroplating.

The two subdivisions of electrophoretic coating are anodic and cathodic processes. This refers to whether the article to be coated is made the anode or the cathode. The chemistry involved in one is in effect the mirror image of the other, but is easier in the case of anodics which accounts for their longer industrial history. Each process has some advantages over the other, the main distinction being that the anodic version is limited to coating some specific metals, (e.g. Aluminium, Gold Plate), whereas the cathodic version will coat any metal.

PROCESS MECHANISM

The material is supplied as a resin concentrate at 50-65% solids which contains all necessary materials to make up a new bath or replenish an existing one. The only additional materials needed are dyes, pigments, matting agents, etc., designed to modify the finish.

This concentrate contains:-

The main resin binder modified to render it water dispersable
A water miscible solvent
A blocked cross linker
Catalyst
Water immiscible solvent
Surface active agents, Emulsifiers
A material to provide the counter ion and give the water
phase a limited low level conductivity

When this material is mixed with water it separates into two phases. The undyed or unpigmented material has a "milk" like appearance due to the light scattering properties of the disperse phase.

Our current processes employ blocked isocyanates as cross-linkers. These materials do not develop isocyanate activity until elevated temperatures are reached and the blocking agent is split off by the action of heat. We have a range of processes employing different cross-linker/blocker systems. The unblocking temperatures vary from 120°C to 147°C. At these temperatures, the activated isocyanates react with the co-resins to form a polyurethane. The inert nature of the blocked isocyanate at room temperature ensures long term stability of the concentrated product and the

made up solution. In some cases the systems also employ a catalyst which speeds up the rate of reaction and this enables good cures to be obtained at quite moderate temperatures. The coatings cure in the range of 130-160°C, the cure times being about 15 minutes at metal temperature.

The resin system can be used alone and unmodified to give clear, transparent, almost invisible coatings which can be used to protect and preserve the underlying metal, e.g. on polished brass, electroplated silver, etc.

The transparent resins can also be dyed to give a wide range of transparent colours. These allow the metal to show through but modify its colour. In this way, silvery white basis metals such as Aluminium, Zinc, Nickel, etc. can be made to look like gold, brass, copper, pewter, etc. or can be given completely artificial colours e.g. green, purple, orange etc.

The resin can also be modified by adding opaque pigments to produce a wide range of solid colours, and black and white. These coatings completely hide the basis metal. They, and indeed the transparent colours, can in addition be modified to produce varying degrees of gloss.

The process can be used in many ways. It can be applied after silver plating to give a clear, invisible coating which prevents tarnishing and resists wear. It means that drying stain problems are eliminated, and much thinner durable coatings can be applied. Cost savings are effected by reducing the typical silver thickness over the bright nickel plate to 0.2 microns. A fully automatic plant using this process has been in operation for over 7 years.

It can also be applied over polished brass. The coating thicknesses applied have varied from about 8 microns on items like photoframes to 20 microns on brass door furniture where it is required to resist wear, weather and sunlight.

A very interesting application is the use of dyed coatings to simulate brass, copper, bronze and gold. These can be applied directly over polished zinc diecastings completely eliminating plating operations. This then avoids the use of toxic chemicals like cyanide, acids, alkalies and metal salts. The problem of spotting out due to chemicals trapped in pores is also eliminated. The speeding up, simplification, and reduction in steps in the process is shown in figures 1, 2 and 3.

Steel can be either coated direct, or where brightening and levelling is required it can be preplated with a bright levelling acid zinc. This can then be coated with brass, copper or gold coloured Clearclad to give the required finish. If solid colours are required, the steel is either coated direct or if maximum corrosion resistance is required then a phosphate pretreatment is applied. One current application is on steel outboard motor parts, which in service are partly immersed in sea water. Coatings carried out on aluminium vary from brass and gold colours to black, white, brown and bronze colours. 25 micron coatings on aluminium extrusions meet all of the requirements of British Standards, BS 4842 and the relevant parts of BS 6496.

Environmental Considerations

Our processes described in this paper were designed to be environmentally friendly. In this respect all of the materials used in the process were reviewed from two main viewpoints:

- 1. Do they prevent a hazard to the environment?
- 2. Are they hazardous to human beings working with them or using the product? The materials used have been constantly reviewed and already some changes have been made in formulations in view of later discoveries about the nature of certain materials. We can confidently say that the materials currently used are all the safest available in both respects.

The second aspect is efficient usage of the materials in the process. This must be considered in several ways.

1. Losses from the coating evaporation and oven curing:
The coating solution is at least 84% pure water. Of the

The coating solution is at least 84% pure water. Of the remaining 16% just over half is resin solids and other non volatiles which coat out on the work and form the final coating. Of the other 8% (maximum) 5% is the water miscible solvent which almost entirely remains in the bath. The remaining 3% is the water immiscible solvent which largely deposits with the resins onto the part (some passes into the water phase due to the coupling effect of the water miscible solvent). When all solvents are extracted from the coating we get a "worst case" measurement of 0.9 lb/gal which renders the process compliant in all areas of all states. In practice not all of this material is evolved in oven curing; some remains in the coating. We are working on improving on even this by using more reactive diluents. Losses from the bath by evaporation are negligible. The vapour pressure of materials used is very low - the most volatile material in the bath is water. Extraction over the bath is not generally necessary.

2. Losses from the coating bath by drag-out

When work exits the coating bath some of the coating solution is dragged out with it. The amount depends on the shape of the work. The drag-out tank immediately following the Clearclad tank employs a spray rinse on entry and exit to ensure efficient removal of the uncoated solids. This material is returned to the coating tank by ultrafiltration. This is shown schematically in Figs. 4,5 and 6. Ultrafiltration is a membrane separation process which separates the disperse phase from the continuous phase. The Clearclad solution is continuously circulated through the ultrafiltration tube. Water plus water miscible and soluble components permeate through the membranes. This permeate is fed into the drag-out tank which flows back into the coating tank thus recovering the dragged out solids. Long term audits on industrial plants have shown that better than 98% of the material added to the tank is coated onto the work. The application efficiency of the process is clearly illustrated by the fact that no rinses running to drain are used after coating.

The ultrafiltration process is also used to continuously purify the coating solution. Without this water soluble contaminants dragged in by the work, on jigs, contaminants in the water, dissolution of fallen components etc will raise the conductivity of the ultra pure water used. This will favour electrolysis over electrophoresis causing gas production and disrupting the coating. This is prevented by passing the permeate through a special ion exchange trap which continuosly removes impurities.

The final rinse in the rinse aid tank which contains a special wetting agent removes much of the water and prevents dewetting. This final rinse aid bath needs changing only every few months. Alternatively it can be slowly bled to drain with the composition maintained by constant top-up.

A standard Ultrafiltration unit suitable for process tanks up to 1200 litres produces 50-60 litres of permeate per hour. To maintain the balance of the bath it is still necessary to dump a little permeate but this is never normally more than 5% of the total permeate production.

If all of the permeate were dumped the maximum possible contaminants in it would be dissolved impurities (anions & cations) 20 ppm, pH 4.2 (mainly due to lactic acid

- a by-product of the anodic reaction), disperse phase solvent 0.4%, continuous phase solvent 4.0% i.e. total solvents 4.4%. The maximum rate of effluent production will be 60 L/Hour. In a typical factory doing even minimal finishing operations one would expect an absolute minimum of 3000/L of water per hour to be continuously discharged from the plant.

This would give effluent water 'contaminated' with a maximum possible of:-

Total solvents $\frac{4.4}{100}$ X 60 = 2.64L in 3000L of water = 0.88 mls/L :

Resin solids :- zero.

Dissolved ions (anions & cations) $\frac{20}{60}$ = 0.33 ppm

In normal operations not more than 5% of permeate is dumped. This reduces the above figures to 0.044 mls/L solvents and 0.016 ppm dissolved ions. The total dissolved ions figure is well below all effluent limits we have encountered. The solvents are all easily biodegradable.

With further improvements we hope to eliminate the dumping of permeate. This will almost practically eliminate water pollution.

We commissioned a study of EPA VOC Regulations by an Environmental Consultant at the University of Illinois. This has reviewed the process against regulations in detail in 10 States (including California and the San Fransisco and L.A. Bubbles). The study has revealed that "In all cases, in all States investigated, in all areas of the State, at all levels of production, for new and existing sources, Clearclad was found to be compliant with all air pollution regulations, with a very comfortable margin".

In addition to this experience has shown that not only can the process meet effluent water regulations, but that it can do so without any effluent water treatment.

Applications of Clearclad Coatings

Some advantages of Electrophoretic coating systems are given below.

- 1. No runs, tear drops, sags or windows in the cured film.
- 2. Superior adhesion.
- 3. Precise thickness control.
- 4. More uniform product therefore more accurate prediction of corrosion life of coated components.
- 5. Excellent coverage with good penetration on to recesses and blind holes.
- 6. Low concentration of solvents in a water based application system thus
 - * No fire hazard
 - * No need for flame proof equipment
 - * Low toxicity
 - * Environmentally friendly

7. Low curing temperature

- *Saves on heating costs
- *Plated parts can be cured on same jigs without damage to jig coatings
- *No drying is necessary therefore the major problems of drying stains is eliminated
- 8. With the ultrafiltration recovery system the ultra high efficiency of the process means that 97-98% of the material purchased is coated on to the components.
- 9. High efficiency means that the process is virtually a closed loop system and is non polluting.
- 10. Use of ultrafiltration means that dragged in impurities are easily removed.
- 11. Coating baths are extremely stable and have very long life. CLEARCLAD APPLICATIONS

A list of current Clearclad Industrial Applications by Industrial Sector, process and function are as follows:

- l. BY INDUSTRIAL SECTOR
 1.1 Door & window furniture i.e. Door & Window handles, locks, fasteners, hinges, etc.
 - 1.2. Tableware & holloware
 - 1.3. Bathroom fittings
 - 1.4. Car alloy wheel
 - 1.5. Bicycle parts
 - 1.6. Other car parts exterior interior underbonnet
 - 1.7. Giftware & fancy goods
 - 1.8. Buttons (mettalic only)
 - 1.9. Trophies (cups, shields, metals etc.)
 - 1.10.Spectacle frames
 - 1.11.Metal parts for leather goods industry (shoe buckles, corners, etc.)
 - 1.12. Metal furniture & metallic parts for non metal furniture
 - 1.13. Kitchenware
 - 1.14. Household goods
 - 1.15.Electrical goods
 - 1.16. Architectural extrusions
 - 1.17. Architectural metal cladding
 - 1.18. Display stands
 - 1.19. Costume jewellery
 - 1.20. Toys

2. BY PROCESS

Clearclad is frequently used over the following plating processes:

- 2.1. Nickel plating
- 2.2. Brass plating

- 2.3. Silver plating
- 2.4. Gold plating
- 2.5. Copper plating
- 2.6. Bronze plating
- 2.7. Bright tin plating
- 2.8. Nickel-chromium plating
- 2.9. Zinc plating

It is also used directly on the following basis metals which have been prepared by - polishing, electro or chemical polishing vibratory or barrel finishing

- 2.10. Brass
- 2.11. Silver
- 2.12. Bronze
- 2.13. Copper -
- 2.14. Aluminium
- 2.15. Zinc Diecast (Mazak Zamac Etc.)
- 2.16. Stainless steel
- 2.17. Some other ferrous alloys

These materials can be forged, extruded, sheet (rolled), cast etc.

3. BY FUNCTION

Clearclad can be used either clear, coloured or pigmented to make it opaque. It can be used indoors or outdoors.

- * It can be used to produce excellent imitations of more materials e.g. dyed to simulate gold or brass; clear over bright tin to simulate silver; flash silver (0.2 micron) to simulate high quality silver plate or solid silver (no tarnishing)
- * It can be used to produce vivid metallic colours which cannot be equalled.
- It can be dyed to simulate copper
- * It can be dyed or pigmented to simulate black wrought iron. In all cases it gives excellent wear and corrosion resistance

A Comparison of Brass plated and Lacquered Zinc Die castings with Brass Coloured Clearclad Coated Zinc Diecastings from an environmental viewpoint

- 1. Traditional Brass Plate & Lacquer (See Fig. 1)
- 2. Brass Coloured Clearclad Coating (See Fig. 2)

Life of Product

The life of the product depends very much on the finish and its ability to stand up

to its environment. Many factors come into this but two important ones are corrosion resistance and wear resistance. Realistic accelerated tests for these and other properties are difficult to devise but two generally accepted ones are

- 1. Salt Spray for corrosion resistance ASTM B117
- 2. Falling Sand for abrasion resistance ASTM D968

The following are comparisons obtained on typical production brass finished zinc diecast handles:

	Brass plated & lacquered	Clearclad Coated
Salt Spray ASTM	24 - 96 hours	250 - 500 hours
Abrasion Resistance	2 - 5 litres	30 - 40 litres

We have customers who are proposing to give 5 and in some cases 10 year guarantees on Clearclad coated parts. We feel it is very safe to say that the life expectancy of our coated handles will be at least three times that of brass plated items. It therefore follows that the requirement to meet market demand is one third when Clearclad is used. This alone will reduce pollution by two thirds before any other considerations are made.

Reclamation of Scrap parts

Re-melting plated zinc diecastings results in contaminated zinc alloy due to the metals with which they have been plated. Re-melting Clearclad coated parts burns off the organic coating leaving the diecasting alloy uncontaminated.

Some figures from an actual manufacturer

The following are some figures from a manufacturer of zinc diecast hardward (handles etc). The thickness of Clearclad coated is 20 microns (0.8 mils) plus/minus 2 microns. This thickness was chosen because on most substrates (including zinc alloy diecastings) the corrosion resistance improves with increasing thickness up to 15 microns (0.6 mils). This thickness is also sufficient to give good enough abrasion resistance to give a long enough life to most components.

This customer consumes 1900 litres/Kgms (Density=1) per year. At 20 microns (0.8 mils) thickness one litre of concentrat(e covers 250 square feet of work. A typical handle is about 0.1 square feet (14.4 sq.inches).

Practical experience over a one year period during which 1900 litres of Clearclad concentrate were used showed the following:-

Handles coated4,750,000

Total solvent added to the tank (all water phase, very little of which goes into the air as VOC)......125 Kgms.

TRAP ion exchange cartridges used52 (Approx.one per working week).

Cost of solvent added plus trap cartridges used as a proportion of total Clearclad materials cost.......4.6%

TOTAL POLLUTION PRODUCED BY THIS PLANT

- 1. VOC evolved on oven curing: Meets strictest regulations.
- 2. Evaporation from tank: Negligible
- 3. Effluent water pollution: Very little no effluent treatment necessary
- 4. Scrap components: Very few
- 5. Disposal of bath material: Not required bath life is indefinite. (In the event of a catastrophe bath is easily treated for disposal).
- 6. Remote pollution e.g. as represented by electricity generation is low. Coating power consumed is very small. Tank heating not necessary. Oven curing is at lower than usual temperatures.
- i.e. Pollution in all respects is LOW!

1. Traditional Brass Plate & Lacquer

Fig 1.

Polish & Degrease

STEP	PROCESS	PROCESS TIME	T/T	HEATING &	POLLUTED AIR EXTRACTED	POLLUTED WATER TO DRAIN (POLLUTANTS
1.	Soak Clean	2.0	0.5	60-70°C	Yes	
2.	Electro Clean*	1.0	0.5	60°C	Yes	·
3.	Running Rinse	0.5	0.5	-	-	Na, Alkali , Silicates, Phosphates Wetters!
4.	. Acid Dip	0.5	0.5	_	_	1 -
5.	Running Rinse	0.5	0.5	-	· <u>-</u>	. Zn,S04, E
6.	Cyanide Copper Strike*		0.5	_	Yes	- 4
7.	Running Rinse	0.5	0.5	-	-	CN',Cu,Na,Alkalai
8.	Copper Plate*	10.0	0.5	-	Yes	-
9.	Running Rinse	0.5	0.5	-	•	Cu, CN' or SO ₄ or Pyrophospha
10.	Acid Dip	0.5	0.5	1 :	-	- 4
11.	Running Rinse	0.5	0.5	-	-	Acid (SO _A)
12.	Nickel Plate*	12.0	0.5	50-60°C	Yes	- 4
13.	Nickel Dragout	0.5	0.5	-	-	-
14.	Running Rinse	0.5	0.5	-	-	Ni,SO ₄ ,Cl,Borates,Brighteners
15.	Cyanide Dip	0.5	0.5	_	Yes	4, 1
16.	Brass Plate*	2.0	0.5	?	. Yes	-
17.	Running Rinse	0.5	0.5	-	-	Cu, Zn,CN,Na,Cl
18.	Neutralize Dip	1.0	0.5	- }	-	-
19.	Running Rinse	0.5	0.5] -)	-	-
20.	Hot Rinse	1.0	0.5	70°C	-	-
21.	Dry .	2.0	0.5	Hot Air	-	-
22.	Lacquer	3.0	0.5	- {	Yes	-
23.	Oven Cure	20.0				
	Total Process Time = 72 Mins.	61.0 +	11.0		T/T - Transfer	Time

^{* 5} Rectifiers employed all using electric power

There are seven water polluting steps, some alkaline, some acid. These have to be treated separately. This is expensive, consumes more power, and produces toxic sludges which have to be disposed of usually in land fills = more remote pollution

Fig. 2.

2. Brass Coloured Clearclad Coating

Polish & Degrease as before

STEP	PROCESS	PROCESS TIME	Т/Т	HEATING	POLLUTED AIR EXTRACTED	POLLUTED WATEL TO DRAIN
1.	Clearclad Coat	2.0	0.5	20-25°C (1)	-	-
2.	Dragout Rinse	0.5	0.5	-	-	-
3.	Rinse Aid Rinse	0.5	0.5	40°C (2)	-	Absolutely minimal
4.	Oven Cure	20.0	-	160°C	Yes	-
	Total Process Time = 24.5 Minutes	23.0	1.5			

- (1) Clearclad Tank may require slight heating or cooling depending upon the ambient temperature.
- (2) Optional: Heating is only to speed up drying and preheat for oven.

Note: The plating process require 7 times as many tanks. This equals approximately the same ration of factory floor space. This in turn reduces requirement for heating or cooling and other associated costs. This also reduces power consumption and remote pollution.

Fig. 3.

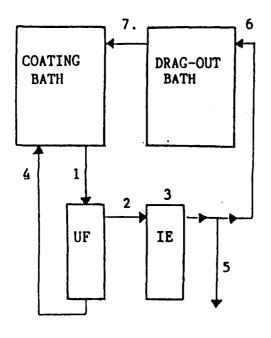
EXAMPLES OF SIMPLIFING SEQUENCE BY USING "CLEARCLAD"

	Surface Finishing	Electroplating		Clearclad Coating		
Substrate	Required	Sequence	Timo	Sequence	Time	
Zinc Diecasting	Drass Plating	Pretreatment - Cyanide Copper - Acid Copper - Nickel - Brass - Spray Lacquer	45 Hin.	Pretreatment - Brass Colour Clearclad	6 Hin.	
Zinc Diecasting	Antiquo Brass	Pretreatment - Cyanide Copper - Acid Copper - Nickel - Brass - Black Nickel - Polishing - Spray Lacquer	45 Hin.	Pretreatment - Blackening - Polishing - Brass Colour Clearclad	Ø Hin.	
Steel	Brass Plating	Pretreatment - Cyanide Copper - Acid Copper - Nickel - Brass - Spray Lacquer	35 Hin.	Pretreatment - Zinc - Brass Colour Clearclad	15 Hin.	
Brass	Gold Plating	Pretreatment - Cyanida Copper - Nickel - Gold	25 Hin.	Pretreatment - Red Colour Clearclad	6 Hln.	
Steel	Gold Plating	Pretreatment - Cyanide copper - Acid Copper - Nickel - Gold	30 Min.	Pretreatment - Nickel - Silver Strike - Gold Colour Clearclad	10 Hin.	
Aluminium	Brass Plating	Not usually done.		Pretreatment - Brass Colour Clearclad	6 Hin.	
Aluminium	Gold Plating	Not usually done.		Pretreatment - Gold Colour Clearclad	6 Hin.	

Note: 1. Pretreatment for electroplating is more complicated and time consuming.
2. Stoving time is not included in both cases.

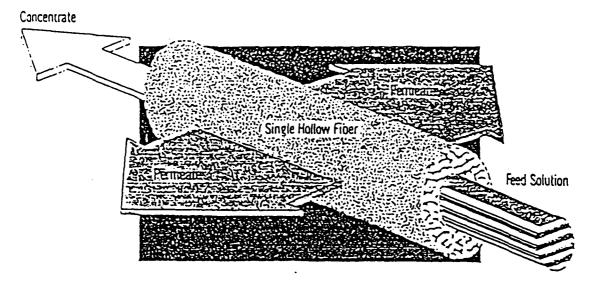
Fig 4.

SCHEMATIC DIAGRAM OF CLOSED-LOOP ELECTROPHORETIC SYSTEM INCORPORATING "TRAP"

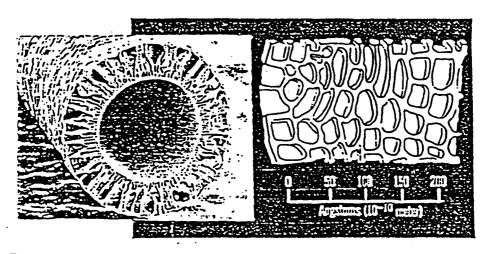


- 1. BATH MATERIAL IS PUMPED THROUGH THE ULTRAFILTRATION UNIT.
- 2. THE FILTRATE (PERMEATE) IS PASSED TO:
- 3. ION EXCHANGE UNIT TO REMOVE METALS AND OTHER IONS.
- 4. THE RETENTATE IS RETURNED TO THE BATH.
- 5. SOME PORTION OF THE TREATED PERMEATE MAY BE DUMPED.
- 6. THE MAJORITY OF PERMEATE MAKES UP THE DRAG-OUT BATH.
- 7. THE INCOMING PERMEATE DISSOLVES AND COUNTER-FLOWS DRAGGED-OVER SOLIDS BACK INTO THE COATING BATH.

In this way the ultrafiltrate and its corresponding retentate are re-combined in the coating bath. On the way the permeate has been purified of foreign contaminants and has been used to reclaim dragged-out solids. In this way, minimal permeate is dumped and the system retains its operating volume. The combination of Ion Exchange and Ultrafiltration in this closed loop concept is called TRAP - Total Reclaim And Purification.

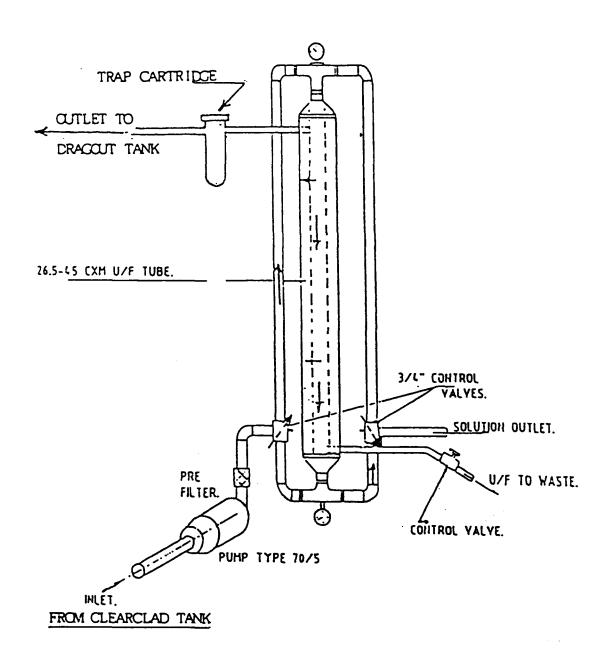


Hollow Fiber principle shell geometry



Exploded view of membrane surface

ULTRAFILTRATION SYSTEM



COATING SOLIDS/NON-VOLATILE MATTER VS. VOLATILE ORGANIC MATTER

Fig. 7.

	AS SUPPLIED/IN BATH	DEPOSIT
COATING SOLIDS	1000	1000
WATER MISCIBLE SOLVENT	700	10
WATER IMMISCIBLE SOLVENT	300	206
VOC "AS SUPPLIED" GM/KG - LB/GAL	500 - 4.16	108 - 0.9

The residual 690 water miscible + 84 water immiscible solvent parts remain in the bath and are "converted" to COD through removal by ultrafiltration.

Electrophoretic coating systems differ from conventional spray and dip paints in that not all of the VOC "as supplied" is volatilised during application or baking. The deposition mechanism excludes the majority of the solvent from the applied coating. This excluded portion of the VOC may be eliminated by ultrafiltration.

TYPICAL BATH CONSTITUENTS OF ELECTROPHORETIC COATING SYSTEMS

Fig. 8.

	% WEIGHT
"VEHICLE" RESIN	5 - 10
CROSS-LINKER	3 - 6
WATER MISCIBLE SOLVENT	3 - 8
WATER IMMISCIBLE SOLVENT	2 - 4
ADDITIVES/EMULSIFIERS ETC.	LESS THAN 2
PIGMENTS/EXTENDERS/DYES ETC.	LESS THAN 10
WATER	BALANCE

Typical CLEARCLAD bath will contain up to 16% of such constituents + balance of water. Auto-body primers may be 30% + balance of water.

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

Water-Reducible Polyurethane Coatings for Aerospace Applications

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Solvent-borne polyurethane coatings traditionally have been the high performance coating of choice for aerospace and military vehicles. State-of-the-art high solids coatings for these platforms typically have a volatile organic compound content of 420 g/l (3.5 lbs/gal). (BMS 1060H, Mil-C-85285B, Mil-C-46168D). The efforts to further reduce VOC have taken many forms. For polyurethane coatings, two-component water reducible polyurethane systems make significant reductions in VOC while maintaining the level of performance expected of traditional polyurethane topcoats.

Introduction

The extreme environments aircraft are subjected to dictates the use of high performance coatings for corrosion protection and camouflage. Aliphatic polyurethane topcoats have long been the coating of choice for aerospace, because they provide excellent flexibility, chemical resistance and exterior durability. Traditionally, this high performance polyurethane coating has been a solvent borne conventional solids system. Aircraft coatings like all other coatings are being required by new government and local regulations to reduce volatile organic emissions. Raw material manufacturers and coatings suppliers have developed high solids and waterborne technology to meet these regulations. This paper will address a new chemistry for low VOC coatings which may have great potential in the commercial and military aerospace markets in particular.

State-of-the art aircraft coatings for military and commercial aircraft are formulated at 420 g/l VOC. These include Mil-C-85285B (Type I), TT-P-2756, Mil-C-83286C (proposed revision) and BMS 1060H. The binder system (which is the largest factor in determining VOC) for these types of coatings make use of a hydroxyl-functional polyester polyol crosslinked with a hexamethylene diisocyanate (HDI) based polyisocyanate to form a urethane linkage. The polyester polyol is a solid at room temperature, requiring a high level of organic solvent to reach practical application viscosities, especially when filled with primary and extender pigments. The polyisocyanate, on the other hand, is a liquid typically 1000 - 4000 cps at 100% solids. It is obvious that modification of the polyol component will have the greatest impact on the level of organic solvent used in the current coating system.

Theory of Waterborne Polyurethane Resins One Component Polyurethane Dispersions

One approach to reduce organic solvent levels in coatings has been to use water as a carrier. This concept has already been applied in one-component aqueous polyurethane dispersions. These are binary colloidal systems made from fully reacted, predominately linear polymers. See Figure 1. Like most organic polymers, polyurethanes are not compatible with water. In order to disperse them in an aqueous media they are modified ionically and nonionically with hydrophilic groups.

A coating made from a one-component polyurethane dispersion would contain pigments, cosolvents and surfactants typically used in waterborne coatings. The VOC of such systems generally ranges from 240-340 g/l. As water and cosolvent evaporate, a film is formed via coalescence. For ambient cure systems, however, commercially available, fully reacted dispersions do not provide the same level of chemical resistance as that of a highly crosslinked solventborne polyurethane.

Considerable work has been done to crosslink the ionic groups of the dispersion with polyaziridines and carbodiimides. A Boeing study formulated a series of polyurethane dispersions and crosslinkers in an attempt to meet the properties of Mil-C-83286B¹. They found that this type of crosslinker made a small improvement in the performance of a one component polyurethane dispersion, but did not meet Mil-C-83286B. Their results showed acceptable corrosion resistance and flexibility, but failures in chemical resistance and high gloss.

Figure 1.
Preparation of a Polyurethane Dispersion

Two-Component Polyurethane Resins
Hydroxy-functional Polyurethane Dispersion

Miles has developed a new family of "polyols" by building hydroxyl functionality into polyurethane dispersions. See Figure 2. A linear isocyanate terminated prepolymer is synthesized from a diisocyanate, polyols and emulsifying agents such a dimethylolpropionic acid (DMPA). The acid groups on the prepolymer are then neutralized with an amine, dispersed in water, and finally chain terminated. If the chain terminator has hydroxylfunctionality, the aqueous polyurethane dispersion will be capped with hydroxyl groups which are available for future reaction.

Figure 2. Hydroxy-functional Dispersion

Water Dispersible Polyisocyanates

As in the case of polyurethane prepolymers, polyisocyanates are not compatible with water. Additionally, the concept of mixing a polyisocyanate with water is unconventional due to its reaction with water. See Figure 3.

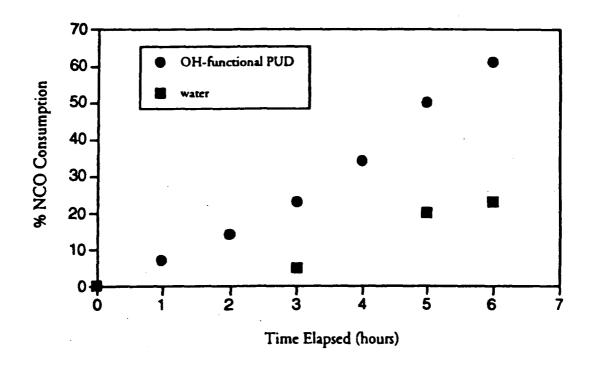
Figure 3.
Isocyanate - Water Reaction

These two potential concerns have been resolved through the development of hydrophillically modified aliphatic polyisocyanates. Depending on the modifying agent, the water dispersability, functionality, and viscosity of the polyisocyanate can be influenced. Although less desirable, reducing the polyisocyanate in an appropriate solvent can, in some cases, improve the dispersion into water.

We know that the uncatalyzed reaction between aliphatic polyisocyanates and water is very slow². We theorize that the polyisocyanate reacts preferentially with the hydroxyl groups of the dispersion over water. Jacobs and Yu³ have monitored the consumption of isocyanate by "polyol" and water over time, noting a trend for the polyisocyanate to react preferentially with the polyol. See Figure 4. As water evaporates from an applied coating, the polyisocyanate particles coalesce with the hydroxy-functional dispersion. We believe that after this coalescence takes place, the isocyanate group comes in close enough proximity with the hydroxyl group to react.

We recognize that some of the polyisocyanate is sacrificed to the water carrier, and as a consequence, we formulate with a large excess of polyisocyanate to insure complete reaction of the hydroxyl groups. We have found optimal property development at NCO/OH ratios of 2.0 and higher. The resultant polymer matrix can be considered a polyurea modified polyurethane.

Figure 4. Isocyanate Consumption vs. Time



Properties

Clear Film Comparisons

To demonstrate the performance range of a two-component water-reducible system, clear films from a conventional solvent borne polyurethane and conventional one-component dispersion were compared to films from a two-component waterborne coating in a common screening test.

Table 1. Clear Binder Comparisons

<u> </u>	2K Solventborne ¹	2K Solventborne ²	2K Waterborne ³	IK PUD4
MEK 2X	200+	200+	200+	20
Pendulum Hardness (sec)	170	23	134	70
Reverse Impact (in-lbs)	160	160	160	160
Tensile Strength(psi)	4900	6200	5755	5700
% Elongation	<5	150	10	160

¹Soventborne HDI polyisocyanate and a highly functional polyester

The results from Table 1 show the increase in chemical resistance (MEK double rubs) of a reactive two-component water-reducible system over a one-component fully reacted dispersion. In fact, this screening experiment suggests the two-component water-reducible polyurethane demonstrates physical and chemical resistance properties of the same order as conventional solvent borne systems.

Pigmented Coatings

Camouflage Topcoats

Our development efforts have suggested that this reactive water-reducible technology would have potential for nearly all high performance topcoat applications. Of particular interest has been military and commercial aircraft topcoats. Commercially viable coreactants were formulated in a series of camouflage and gloss coatings, and tested toward the critical requirements of Mil-C-85285B, Type I, Mil-C-83286B, and commercial BMS-1060H. Factors such as NCO:OH ratio, OH-functionality, coreactant molecular weight, polyisocyanate modifiers, surfactants, and manufacturing procedures were varied in early formulation development. The results of experimental designs and confirmatory experiments were used to design formulations for aerospace applications. Responses measured for these experiments include impact flexibility, low temperature flexibility, Skydrol resistance, water resistance, adhesion, hydraulic and fuel oil resistance and gloss.

²Soventborne HDI polyisocyanate and a tri-functional polyester

³Reactive two-component waterborne system

⁴Aqueous polyurethane dispersion

Table 2 is a portion of a screening experiment used to determine appropriate NCO/OH ratios for a camouflage military aircraft topcoats.

Table 2.
Water-reducible Camouflage Coating

NCO/OH	1.5	2.0	2.5	3.0	3.5
GE Impact	20	20	20	20	10
Low Temp Flex ¹	· pass	pass	pass	pass	pass
Mil-L-23699	fail	pass	pass	pass	pass
Skydrol ² Fluid	blistered	blistered	3 Δ pencil	1 Δ pencil -	1 Δ pencil
Resistance					

¹ Bend over 1" mandrel at -65°F

Several coatings formulations designed to meet the different requirements for Air Force, Navy and commercial specifications were developed based upon this type of characterization. The following is an example of a camouflage aircraft topcoat formulation and test results according to Mil-C-85285B, Type I. Bayhydrol XP-7044 is the OH-functional polyurethane dispersion and Desmodur XP-7007 is the water dispersible HDI-based polyisocyanate. An NCO:OH ratio of 3.0 was taken from Table 2 and used in the following initial formulation because it met the chemical resistance and impact flexibility requirements for military aircraft. The VOC of the final system is 211 g/l (1.76 lbs/gal).

² Skydrol is a registered trademark of Monsanto. Δ pencil is the drop in pencil hardness after 7 days immersion in Skydrol 500B fluid. 2 Δ pencil with no blistering is considered acceptable.

Two-Component Waterborne Aircraft Topcoat

#191-53

RAW MATERIAL	WEIGHT	VOLUME	WEIGHT SOLIDS	VOLUME SOLIDS	WEIGHT WATER	SUPPLIER
COMPONENT I						
Predisperse on Cowles N	lixer:					
Bayhydrol XP-7044	84.67	9.61	33.87	3.51	40.64	MILES
De ionized Water	162.18	19.47	0.00	0.00	162.18	
Byk 321	4.32	0.56	2.17	0.28	0.00	Byk-Chemie
Tinuvin 292	2.89	0.35	2.89	0.35	0.00	Ciba Geigy
Tinuvin 1130	2.89	0.29	2.89	0.29	0.00	Ciba Geigy
10% Black Tint Paste	11.30	1.24	5.92	0.60	5.24	
TiO ₂ R-960	57.74	1.73	57.74	1.73	0.00	DuPont
Syloid 234	54.06	3.24	54.06	3.24	0.00	Grace
Letdown:						
Bayhydrol XP-7044	350.18	39.75	140.07	14.49	168.08	MILES
FC-430 (20% in H ₂ O)	28.50	3.34	5.70	0.60	22.80	3M
Sand Mill entire Compos	nent I to at le	ast 5 Hegman	1			
COMPONENT II						
Desmodur XP-7007	111.36	15.31	111.36	15.31	0.00	MILES
Exxate 600	_37.12	_5.10	_0.00	0.00	_0.00	Exxon
Total	907.21	100.00	416.67	40.40	398.94	

Test Results

Form	ulation #191-53	Mil-C-85285B, Type I Control
Initial Viscosity #4 Ford	25"	28"
4 Hour Viscosity	33 "	32 "
VOC	211g/l	420 g/l
60° Gloss	6.0	4.5
Scrape Adhesion to Primer	6 kg	5 kg
7 Day Immersion in:		-
Mil-H-83282*	$\Delta E = 1.3$	$\Delta E = 0.7$
Mil-L-23699*	$\Delta E = 3.1$	$\Delta E = 2.4$
GE Impact	20%	40%
Low Temp Flex 1"	Pass	Pass
1 Year Florida Weathering	$\Delta E = 0.63$	N/A

^{*}AE is the measure of color change in CIELAB, Illumunant C color space. It is used as a comparative measure of fluid resistance.

When compared to the solvent borne control at 420 g/l, the two component water borne system gives comparable performance at less than half the VOC. We are currently pursuing field trails of this material on operational aircraft.

Gloss Topcoats

One of the drawbacks to some waterborne systems is the ability to achieve high gloss. A binder system containing Bayhydrol XP-7044 polyurethane dispersion and Desmodur XP-7007 polyisocyanate performs well in camouflage systems, but it is difficult to achieve a 60° gloss greater than 80. Similar formulations utilizing experimental resins designed for higher gloss, however, demonstrate encouraging preliminary results for military gloss topcoat and commercial topcoat applications at VOC's as low as 120 g/l (1.0 lb/gal).

In the first system, an experimental polyisocyanate (EX-P) has been modified to be even more water dispersible than Desmodur XP-7007. This new polyisocyanate does not require reduction in cosolvent for incorporation in water, and when reacted with XP-7044, films are higher in gloss and more flexible. A third system has made use of a new water dispersible alkyd (WRA) designed for high gloss. Films made from the WRA/EX-P demonstrate high gloss, good DOI, and excellent chemical resistance. Initial coatings systems have been tested for gloss, flexibility and Skydrol fluid resistance as well. See Table 3.

Table 3.
New Resins for Aircraft Topcoats!

	XP-7044-7007	XP-7044/EX-P	WRA/EX-P
VOC	211	128	127
60°/20° Gloss	71/33	85/58	88/78
DOI	60	82	90
7 Day Skydrol Fluid	pass	fail	pass
Resistance ²			•
30 Day Skydrol Fluid	fail	fail	pass
Resistance ³			•
GE Impact ⁴	20%	40%	20%

¹ All coatings tested were pigmented with TiO2 at a pigment to binder ratio of 0.7.

Summary

Today's aircraft perform very different missions subjecting them to a wide range of environments. A military fighter for instance, requires a coating that is very flexible, usually low gloss, and of moderate chemical resistance. A commercial airliner, on the other hand, requires a coating which provides excellent chemical resistance to such fluids as Skydrol, high gloss, and moderate flexibility.

² Tested over epoxy primer Mil-P-23377. Failure is defined as a decrease in hardness of greater thane 2 pencils.

³ Tested over epoxy primer BMS 10-79.

⁴ Tested direct to bare anodized 2024-T0 aluminum as in Mil-C-85285B.

The common requirements these types of coatings share are light stability and low VOC. The performance data described in this paper demonstrate a level of performance of the same order as traditional aircraft topcoats of all types while reducing VOC by more than 50%. Products such as the OH-functional polyurethane dispersions demonstrate the excellent flexibility needed for military aircraft, while we believe the newer generations of modified polyisocyanates and WRA's provide high gloss and excellent chemical resistance demanded by commercial aircraft applications.

Our future efforts will be directed at formulating and testing this technology in all markets including the aircraft industry. Future development will be 1) to continue researching resin compositions and manufacturing techniques to attain Miles' goal of very low and zero VOC coatings 2) to more fully characterize weather resistance through accelerated methods and inprogress outdoor exposures and 3) to pursue field trials of laboratory-proven coatings in cooperation with coatings manufacturers to ultimately determine coating performance in a real-life exposure.

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SESSION 8

APPLICATIONS 1

PAPERS PRESENTED:

"Water Based and UV-Cured Coatings for Plastics"

by

Edwin C. Laird

Coatings Resource Corporation

Huntington Beach, California

"Water-Borne Lacquers for Aluminum Foil"

bν

William F. Marwick

Alcan International Limited

Banbury Laboratories

Banbury, England

"Lower-VOC Coating System Conversion Costs for the Wood Furniture Industry"

by

Mary-Jo L. Caldwell

Midwest Research Institute

Cary, North Carolina

"Development of Ultra-Low VOC Wood Furniture Coatings"

by

Eddy W. Huang

Center for Emissions Research and Analysis

City of Industry, California

and

Larry Watkins

South Coast Air Quality Management District

Diamond Bar, California

and

Robert C. McCrillis

U.S. Environmental Protection Agency

Air and Energy Engineering Research Laboratory

Research Triangle Park, North Carolina

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

Water Based and UV-Cured Coatings for Plastics By Edwin C. Laird, President - Coatings Resource Corp.

I. HISTORY

The evaporation of solvents from coatings has long been determined to be a cause of smog. The formation of smog has been directly attributed, in part, to the reaction of organic hydrocarbons with NOx and sunlight to form ozone in the lower strata. Solvents were segregated by their photochemical reactivity. Until recently, these solvents were limited to allowable prescribed levels in coatings. Recently, regulations have indicated that <u>all</u> solvents are smog precursors. Thus, all solvent usage has been regulated, and consequently, their usage has decreased.

Prior to 1966, coatings for plastics consisted of extremely high levels of aromatic solvents, branched ketones, and chlorinated solvents. These solvent rich coatings yielded volatile organic contents (VOC's) in excess of 700 g/l. As a result of the above cited regulations, the average VOC levels of most coatings for plastics have decreased by over 60% to a level of 275 g/l.

It should be noted that although some industries have been able to reduce VOC levels to this extent, others have not been able to achieve the same results. To a great extent, due to the lack of polymer technology advancement, some coatings for plastics, such as thin film applications used in vacuum metalizing, still emit a high level of VOC.

The quest for lower VOC emitting coatings has progressed along two major lines of technology. These two lines are waterbased systems and ultraviolet radiation cured (UV cured) systems. Both of these lines of coatings technology, although in their infancy when compared to the old-style solvent based coatings, have yielded replacements to the conventional solvent based coatings. In some instances, these products have not only matched the solvent based coatings in performance and economics, but have actually exceeded them.

II. WATERBASED SYSTEMS

The trend to waterbased vehicles constitutes perhaps the single most important development in the field of plastics finishing during the last decade. As of 1970, this market had been, with very few exceptions, almost solely restricted to polymer vehicles

Ed Laird, Coatings Resource Corp. Waterbased and UV-Cured Coatings for Plastic

supplied in solvent. Now, less than two decades later, waterbased polymers comprise 20% of the vehicles used by the plastics finishing industry.

Waterbased polymers have developed along three major lines: styrene-acrylic emulsions, acrylic emulsions, and polyurethane dispersions. These systems have been shown to be substrate dependant. A coating that adheres to styrene may not adhere to ABS. Thus, a careful evaluation of polymer systems is necessary to determine the optimum performance properties that are desired.

Based upon extensive testing in the plastics industry, the styrene-acrylic emulsions demonstrate the best overall stability and adhesion to a multitude of plastics. This is due, in part, to the styrene component of the polymer. However, if film clarity and whiteness is of concern, this same styrene component may be detrimental to the overall finish. When exposed to ultraviolet light, the styrene component yellows, thereby detracting from the film clarity. If mar resistance is a desired characteristic, then styrene-acrylic resins would be a logical choice due to the hard film produced by the resin.

Acrylic emulsions furnish coatings manufacturers with a broad array of performance properties including high gloss, color and gloss retention, and the ability to withstand the degrading effects of water and harsh industrial chemicals. Best of all, the coatings manufacturer and user obtains these properties while avoiding highly toxic and flammable petrochemical solvents.

Polyurethane dispersions provide unique qualities normally associated with solvent based two component urethanes, while avoiding highly toxic and flammable petrochemical solvents, much like acrylic emulsions. Some of the properties associated with polyurethane dispersions include superior chemical resistance, light fastness, and adhesion to various plastics. Polyurethane dispersions are currently used in automotive, aerospace, and business machine finishes. Although the dry times of polyurethane dispersion products rivals those of other polymer families, the polyurethane dispersion coatings required a little more time to achieve their properties. In order to accelerate the attainment of these properties, chemical crosslinkers can be used.

Each of the above cited systems require coalescing solvent in order to achieve their optimum performance. As a general rule,

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Waterbased and UV-Cured Coatings for Plastic

the harder the polymer, measured by its minimum film forming temperature (MFFT) and glass transition temperature Tg, the more coalescent that is needed. Additionally, the evaporation rate of these coalescing solvents must be slower than that of water. This is of vital importance in order to mitigate the effects of humidity. If the relative ambient humidity is high, the evaporation rate of the water in the coating is retarded. This creates a condition in which the water is the last volatile to evaporate from the coating. As a result, improper film formation is likely to occur. Thus, the coalescing solvent serves a critical purposes. It softens the polymer matrix so that it fuses the polymer particles to each other and to the substrate.

The transition from solvent to water systems has not gone without complications. Most industrial coatings manufacturers and users learned to work with solvent-borne vehicles and are far more familiar with them than with waterbased emulsion polymers. natural tendency is for the formulator and user to handle and formulate these polymers in the same manner as solvent-borne vehicles. This approach may not produce optimal coating on Consequently, the manufacturer and users were plastic parts. forced to adapt their processes in order to accommodate the new in coatings. But, technology as a result these of accommodations, have new coatings emerged that environmentally friendlier and simultaneous yield substitute, if not superior coatings for the plastics industry.

III. ULTRAVIOLET RADIATION CURED (UV CURED)

Ultraviolet Radiation (UV) cured coatings are comprised of monomers (a single polymeric unit), oligimers (very short chained polymers), and photoinitiators. These coatings need to be exposed to light energy with wavelengths between 240 and 400 nm. These coatings cure extremely fast at relatively low temperatures. The entire surface of the part must be exposed to the light source in order for the reaction to occur. Coatings of high gloss, high solids, zero VOC, with lower energy costs than thermal cured systems are readily available.

Monomers are used as reactive diluents since they are inherently low in viscosity. Their degree of functionality imparts different properties to the final film. The greater the degree of functional groups that a monomer has, the more crosslinking that occurs. This translates to increased hardness and decreased flexibility. Monofunctional monomers, those with one functional

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Waterbased and UV-Cured Coatings for Plastic

group, provide the greatest viscosity reduction.

These materials are the basis for health concerns related to UV curable materials. Using standard hygienic practices that are employed when using any coating is sufficient to mitigate any sensitization that may occur as a result of monomer exposure.

Oligimers are the main polymeric materials used today. They have a small degree of functionality that allows them to react with each other and the monomer. Generally, they are difunctional (two functional groups) low molecular weight polymers with a backbone comprised of either acrylic, urethane, epoxy, or polyester. The choice of polymer is dependent on the desired end-use. All of these resin types impart greater strength, hardness, solvent resistance, and gloss than their solvent or waterbased counterparts.

Photoinitiators are, as the name implies, chemicals that initiate the curing reaction upon absorption of the UV light. The selection of the photoinitiator is crucial. This minor component will dictate whether the coating cures and at what wavelength. The entire UV spectrum can be covered by a variety of photoinitiators. A curing package is developed by coupling the wavelength of the light emitted by the UV lamp with the wavelength absorption characteristics of the photoinitiator.

Pigmented coatings are more complex than clear coatings. This is due, in part, to the reflection of non-absorbed light. Pigments, as well as other fillers, absorb radiated light. Each pigment has its own pattern of UV absorption that needs a photoinitiator package and lamp designed for it. White UV curable coatings are extremely difficult to cure, as white is the reflectance of all light, and the photoinitiators used have a tendency to yellow with time. UV coatings are intrinsically higher in viscosity and, in many cases, need to be reduced with solvent in order to be applied, thus increasing their VOC emissions.

IV. CONCLUSION

Low VOC coatings for plastics have improved exponentially in the past decade. For many industries, these have proven to be the

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salvation in light of the ever increasing regulatory controls. in most cases, Waterbased coatings have become, replacement for solvent based lacquer systems. Research on polymers continues, looking to produce hard durable materials even lower VOC levels. Additives are constantly being created to enhance properties of coatings on exotic substrates such polysulphone, PEEK, and high temperature composites. The future for waterbased coatings indicates that it will experience ever-increasing demand, as more and more production processes substitute waterbased for solvent based coatings.

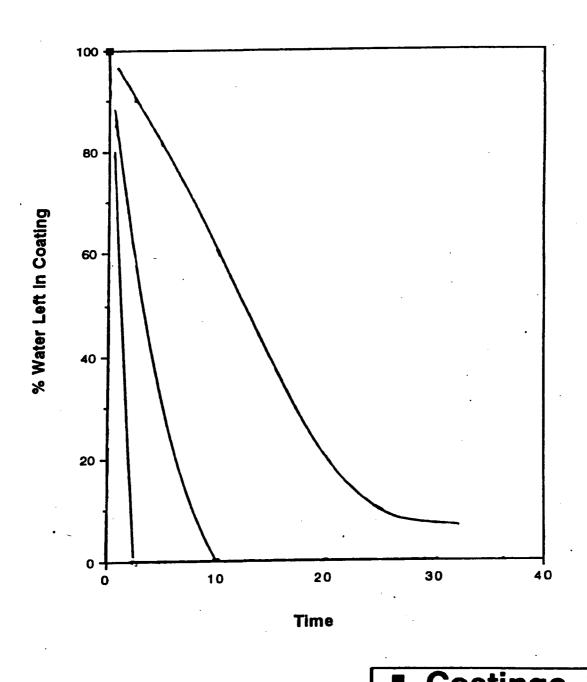
Ultraviolet curing technology work will continue on the curing of three dimensional parts, lowering of the expense associated with the light sources, increasing the power of these light sources, and developing pigmented coatings. Resin companies have developed waterbased UV resins that use water, rather than VOC emitting solvents, to reduce the viscosity of the system. This necessitates some heat to evaporate the water, but application becomes much easier. Simultaneously, this would reduce the amount of monomer that is needed in the system.

Even with these advancements, some coatings for plastics cannot be reformulated to achieve these same results. In these cases, the manufacturer must look towards emission control equipment in order to comply with the current emissions regulations. If this approach is taken, the capital costs of installation and operation must be given serious consideration along with maintenance costs required to keep the equipment in proper working condition.

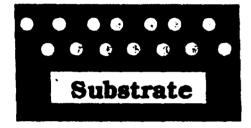
In conclusion, it must be noted that although great advances have been attained in low VOC and zero VOC coatings for plastics, it is still a technology that is in its infancy. It is hoped that the tremendous growth in this technology will continue to where all plastics can and will be coating with low VOC and zero VOC coatings.

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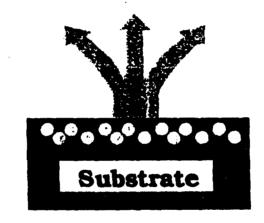
Effect of Relative Humidity on the Evaporation Rate of Water from Waterbase Coatings



Film Formation of Waterborne Coatings



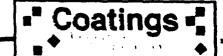
Waterborne coating on surface



Water evaporation yields close-packed spheres with solvent filled voids

Substrate

Further evaporation and polymer deformation yields continuous film



(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

Water-borne Lacquers for Aluminum Foil

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1. INTRODUCTION

Alcan rolls and converts aluminum foil in many countries worldwide. Facilities are in Louisville, Kentucky and in Australia, Brazil, Germany, Japan, Scotland and Switzerland. Particular attention is being paid to VOC emissions from these plants. Low gauges of aluminum are coated with lacquers, and thus the quantities of organic solvent used are comparatively great when compared to painting operations carried out on other aluminum semifabricates such as building siding or extrusions, if the calculation is on the basis of solvent use per tonne of metal. Water-borne lacquers offer an environmentally beneficial alternative to the use of conventional solvents, and environmental legislation in several countries (e.g. U.K., Australia) is following the example of the United States in encouraging the use of water-borne lacquers.

Not all converted foil products can be successfully lacquered with water-borne lacquers. In particular, food packaging products for which a sterilisation step in required, and where an interior-lacquered aluminum surface is sterilised after filling with the food contents, need a combination of chemical resistance and lacquer toughness which is very hard to achieve. Similarly, packaging products for which the lacquer has to provide both a heat-seal action and then resist a pasteurisation step, need a combination of properties which are mutually conflicting for water-borne resins. For these sorts of products, thermosetting vinyls and epoxies will be very hard to replace.

Some products, however, are relatively easy to lacquer with water-borne lacquers; one of these is cigarette bundling foil, the interior packaging of cigarettes. Alcan makes this product in four of the above countries, and this paper discusses technical issues arising in the changeover to water-borne lacquer for this product, both in terms of the coating formulation and the coating process.

2. PROPERTY REQUIREMENTS FOR CIGARETTE BUNDLING FOIL

Cigarette bundling foil is a laminate of 22 g/m² paper and 7 micron aluminum foil, gummed together with a silicate adhesive. The function of bundling foil is primarily to assist in the high-speed packaging operation, the cigarettes being first "bundled" in the foil and the carton being folded and glued around the bundle. The product is particularly suitable for this operation because of the "dead-fold" characteristic of the foil-paper laminate, and the chief function of the lacquer is to impart the correct frictional characteristic to the foil surface, to enable the machinery to handle it properly. There is a minimal requirement for water resistance, and of course an absolute requirement for an absence of off-taste from the lacquer. Tobacco companies in the U.K. mostly use a gold lacquered foil, while in the U.S.A. most lacquer is clear. Color and gloss are therefore properties which often need to be closely controlled.

3. CONVENTIONAL LACQUER: PRODUCT & PROCESS CONSIDERATIONS

3.1 Product considerations

The conventional lacquer which has been used for many years for cigarette bundling foil is based on nitrocellulose resin, dissolved in ethanol with some ethyl acetate added, and containing plasticiser and solvent-soluble dyes.

Gloss and transparency of the nitrocellulose lacquers are very good. Water resistance is also very good, indeed this property is far higher than the cigarette companies actually need. Retained odor is potentially a problem for these lacquers, because if there are any high boiling-point solvents presert, they are difficult to remove completely from the coating. Historically, this occurs very rarely.

3.2 Process considerations

Gravure-applied lacquers need to have an on-machine viscosity of 20 to 30 seconds (zahn 2 cup). With a nitrocellulose lacquer this is achieved at about 15% solids in ethyl acetate/alcohol. The dry coatweight applied is approximately 1 - 1.2 g/m², so that between 7 and 8 ml/m² of wet coating need to be applied. This implies a relatively coarse gravure roll, perhaps 100 lines/inch with 50 micron cell depth. Coating with these parameters is easy from a production point-of-view; control of color intensity is not difficult, coating machines can run faster than 400 metres/minute, and coating heads are easy to clean because of the ready dissolution of the lacquer in solvents. Nitrocellulose lacquers dry readily, but 6 - 7 ml solvent is given off per square metre of foil. The high flammability of the solvent mixture means that a large airflow is needed in the driers; the Lower Explosion Limit for the solvents is 2%, so that a large amount of air has to pass through and be heated up. Some of Alcan's plants have been obliged by local legislation to install incinerators to burn these solvent vapors, and this means both high capital and running costs.

4. WATER-BORNE LACQUER: PROCESS & PRODUCT CONSIDERATIONS

4.1 Product considerations

4.1.1 Resins. Water-borne lacquers can be based on acrylic, sulphonated polyester or polyurethane resins; there are also some oxidizable alkyds and epoxy-esters for use where alkali resistance is important. The polyurethanes and sulfonated polyesters both have properties which make them preferable to acrylics in some applications, but the work reported here focuses exclusively on acrylics; they will remain the cost-effective choice for many applications. The essence of formulating a lacquer with water-borne acrylic resins is to build in a mechanism whereby drying is irreversible. In this way a stable solution or dispersion becomes a water-resistant film on drying. The mechanisms employed are as follows:

- loss of neutralising ammonia or amine on drying
- * coalescence of dispersed droplets.

Acrylic solution resins have enough acid groups to dissolve completely in alkaline water, giving a clear, viscous solution; they dry only by the first mechanism. Acrylic dispersion resins, which are polymerised from sub-micron dispersed droplets of monomer, have a higher molecular weight and only enough acid groups to stabilise the dispersion. They dry by both mechanisms. These two classes of resin impart both desirable and undesirable properties to the lacquer: For cigarette bundling foil, the lacquer needs to be coatable at quite high solids, so that the quantity of water to be dried off is minimised and the coating machine speed is not compromised. The dried film needs to have some water-resistance. Dispersion resins are thus the obvious choice for the resin vehicle. However, some degree of redispersibility at the coater tray is also important, otherwise the gravure roll cells will fill with coalesced or dried lacquer, especially if the gravure roll stops momentarily whilst it has lacquer on it. For this reason, a blend of dispersion resin with some solution resin is best.

SOLUTION RESINS

DESIRABLE

UNDESIRABLE

redispersibility at coater

high viscosity slow to dry

poor alcohol & water resistance when dry

DISPERSION RESINS

DESIRABLE

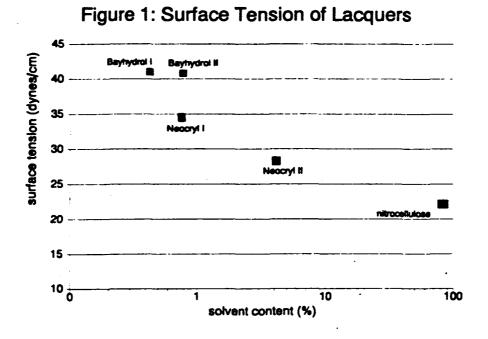
UNDESIRABLE

low viscosity fast drying

limited redispersibility at coater

water resistant, sometimes alcohol resistant, when dry

- 4.1.2 Amine neutraliser. Choice of neutraliser also influences the film-forming process and the drying rate. Clearly, a volatile base such as ammonia or morpholine will give the fastest drying but also the greatest risk of cell-blocking on the gravure roll. An alkanolamine with a lower volatility reverses this balance. Correct selection depends on machine conditions.
- 4.1.3 Coloration. Conventional nitrocellulose lacquers for "gold" foil brands predominate in the U.K. They contain dissolved dyes and are transparent when dry. Replicating these gold colors with water-borne lacquers is difficult; one can use pigment dispersions designed for aqueous systems (e.g. Microlith WA series, Ciba-Geigy Pigments Ltd.) but the transparency of the dried lacquer is reduced, especially if the foil is viewed at a glancing angle. Alternatively, it is possible to incorporate some dyes (e.g. Savinyl, Sandoz Chemicals Ltd.) in stable dispersions, and this gives excellent transparent shades. The Savinyl dyes need first to be dissolved in cosolvents which can then be let down with acrylic solution resins, with water and finally with emulsion resins; many of the latter are only marginally compatible with the dye-cosolvent mixtures. Useful cosolvents for the Savinyl dyes include diacetone alcohol, acetylenic alcohols and isopropanol.
- 4.1.4 Cosolvent. A small amount of an alcohol or glycol ether cosolvent has a pronounced effect on the wetting action of water-borne lacquers. Inevitably, the surface tension of these is higher than for the corresponding alcohol-based nitrocellulose lacquer. This makes water-borne lacquers more sensitive to the substrate surface. Good coating quality is obtained from an annealed foil surface. At Alcan, conventional practice is to anneal the coils for 34 hours at 300°C; this removes organic contaminants effectively. Figure 1 shows the effect of some formulation changes on lacquer surface tension.



This was measured on a Cahn Microbalance using the Wilhelmy plate method; glass slides of dimensions 24mm x 32mm x 0.15mm were lowered into lacquer samples at 40 microns per second.

```
Key to Figure 1:
"Bavhydrol I":
                Bayhydrol LS2884 aqueous polyurethane resin (Bayer AG, D5090 Leverkusen, Germany)
                Microlith yellow 2RWA pigment (Ciba-Geigy Pigments, Manchester, U.K.)
                Microlith scarlet RWA pigment (Ciba-Geigy Pigments, Manchester, U.K.)
              (Surfynol TG surfactant (Air Products & Chemichemicals, Inc., Allentown, PA)
       0.42% { Isopropanol
                water
"Bayhydrol II": Bayhydrol LS2884 aqueous polyurethane resin
                Microlith yellow 2RWA pigment
                Microlith scarlet RWA pigment
       0.77%
                Isopropanol
                water
"Neocryl I":
                Neocryl BT67 acrylic resin emulsion (ICI resins b.v., Waalwijk, Holland)
                Microlith yellow 2RWA pigment
                Microlith scarlet RWA pigment
       0.77%
                Isopropanol
                water
```

Neocryl II: as Neocryl I but with more isopropanol.

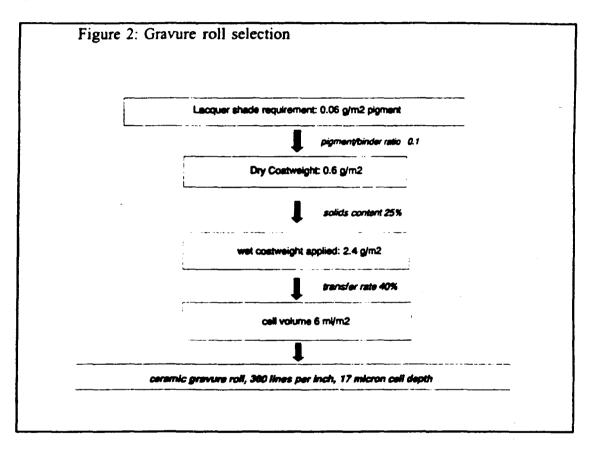
The general pattern is that, for any water-borne resin system, the addition of a few percent of solvent improves the wetting. Fair comparisons between one resin and another are difficult, because some are supplied with small amounts of solvent already present.

4.2 Process Considerations

We have found that efficient coating with water-borne lacquers requires a number of changes to the process. Firstly, the higher solids content (approx. 30%) of water-borne lacquers at viscosities suitable for gravure coating (20 - 30 seconds, Zahn 2 cup) makes a lower wet filmthickness desirable for both economy of lacquer and drying speed. Secondly, the irreversible film-forming characteristic of the acrylic dispersions makes coating head control very important; drying of the lacquer in the gravure cells has to be prevented by keeping the roll turning in the tray even during a machine stop. These and other process considerations relating to water-borne lacquers have been widely recognised. Perhaps less well known is the use of fine ceramic gravure rolls to deposit uniform wet films at very low coatweights. These have been utilised with very encouraging results. The sequence involved in ensuring that the required dry coatweight (0.6 g/m²) is applied is shown in figure 2. In this sequence it may be seen that the desired color shade requires a pigment coatweight of 0.06 g/m² dry coatweight, which for the candidate formulation requires 0.6 g/m² dry coatweight of the complete lacquer. The lacquer reaches the correct viscosity for coating at 25% solids, and has a specific gravity of 1, so 2.4 ml/m² wet coatweight needs to be applied. The fine ceramic gravure roll has a transfer factor of about 40% when coating onto bare aluminum foil; that is to say, the wettability and surface roughness of the foil in relation to the wettability of the chrome oxide ceramic result in about - 40% of the contents of a cell full of lacquer being transferred to the foil.

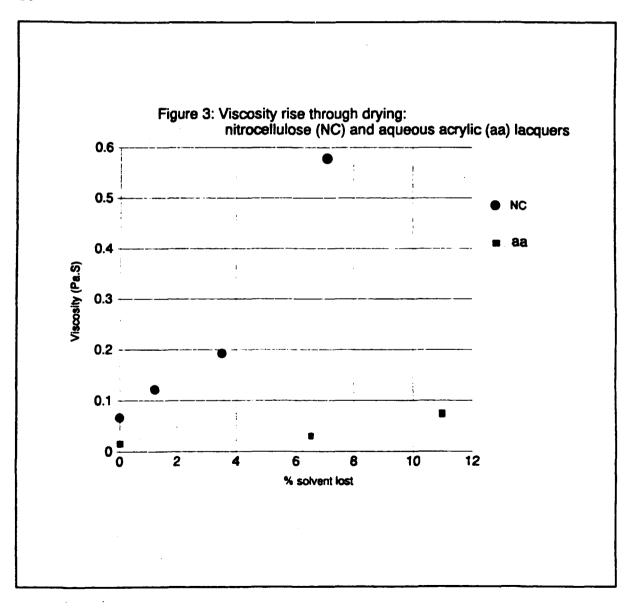
It is not widely known that the transfer rate of water-borne lacquers from these rolls to aluminum foil is so low; correct knowledge of this parameter is of course essential if the correct roll engraving is to be selected.

Thus a gravure roll with a cell volume of 6 cubic centimetres per square metre is needed; this implies an engraving of the order of 17 microns cell depth and 360 lines/square inch. This very fine gravure roll gives a welcome benefit in that the spread or lay of the lacquer coating has been found to be excellent, indeed better than that achieved routinely from the nitrocellulose lacquer. The laser-engraved ceramic material ("Ucarlox", Praxair Surface Technologies Ltd., Swindon, U.K) combines wear resistance with an accurate consistency of cell dimension across the web; this is of course essential for a colored lacquer, if shade is to be kept within specification at such a low coatweight.



A comparison with the process parameters required for the nitrocellulose lacquers (see 3.2 above) shows that a wet coatweight of 2.4 ml/m² is applied in the case of these water-borne lacquers, as opposed to 7 - 8 ml/m² for the solvent-borne nitrocellulose. This low wet film thickness overcomes the drying problem, and it also minimises the environmental effect of the few percent of cosolvent which are included in the formulation to ensure good wetting of the substrate. Finally, a cost reduction vis-a-vis the standard nitrocellulose lacquer is clearly obtainable, at least in terms of material costs, since the dry coatweight has been halved and the two lacquer types are broadly comparable in cost on a dry solid cost basis. Long-term production experience will be needed before a reliable calculation can be made, which also includes cost changes arising from the process changes.

The excellent spread of the water-borne lacquer - referred to above - deserves further analysis; it relates to the ease with which the dots of lacquer transferred to the foil surface can enlarge and merge before they become immobilised through loss of solvent. To demonstrate the difference between the standard nitrocellulose lacquer and a typical water-borne acrylic, the two formulations were made at a number of higher solids contents than the actual on-machine formulations, and the viscosities were measured on a Bohlin "Visco 88" viscometer. The results are expressed in Figure 3 as viscosity against the percentage of solvent lost from the initial concentration. Expressing the results in this way removes any consideration of relative evaporation rate, since for any lacquered foil passing through a drying oven, the solvent loss must progress from 0% to essentially 100% from coating head to coil-up, and this is the time during which dot-enlargement has to take place. It is clear that the rise in viscosity for the nitrocellulose lacquer is very sharp; that is why such lacquers can so easily give a mottled appearance.



4.2.1 Ultrasonic Cleaning. A process consideration which was mentioned in 3.2 above was the easy cleanability of the gravure roll when solvent-borne lacquer is used. The water-borne lacquers can give problems in this respect, the drying being much less reversible than is the case with nitrocellulose lacquers, even when the formulation contains carefully chosen combinations of resin types, amine and cosolvent. With this in mind, an on-machine ultrasonic cleaner has been installed. The resonator (Telsonic AG, Bronschhofen, Switzerland) is in the form of a tube which extends the full length of the gravure roll, and is located in the lacquer tray underneath the bottom of the roll. The tray bottom is semicircular in profile, such that ultrasonic waves are reflected upwards onto the roll surface. The tray can be drained of lacquer and refilled with a mild alkaline cleaner prior to switching on the ultrasonic resonator. The installation eliminates the need to remove cylinders from the machine for cleaning; this was felt to be important, because the brittle nature of the ceramic gravure roll makes it vulnerable to mechanical damage during handling. Long-term experience of the use of the ultrasonic cleaner has yet to be gained, but it is certainly effective.

5. CONCLUSIONS

The change from solvented to water-borne lacquers requires some changes to the coating process, and does not give a cigarette bundling foil with identical properties to the original product. However, this development work at Alcan has convinced us that there are as many positive as negative property changes; in addition there is not only an environmental benefit but also a potential cost saving. Water-borne lacquers are most useful where local regulations permit small quantities of cosolvents (alcohols or glycol ethers) to be included.

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LOWER-VOC COATING SYSTEM CONVERSION COSTS FOR THE WOOD FURNITURE INDUSTRY

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NOTE: Although the research described in this technical paper has been funded wholly or in part by the U. S. Environmental Protection Agency contract 68-D1-0115 to Midwest Research Institute, it has not been subject to the Agency's review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

BACKGROUND

During the manufacture of furniture, volatile organic compounds (VOCs) are emitted from the coating operation. These VOCs can contribute to the formation of ozone and exceedances of the National Ambient Air Quality Standard for ozone. In order to attain the ozone standard in many parts of the nation, emissions of VOCs must be reduced.

The U.S. Environmental Protection Agency (EPA) is currently developing a control techniques guideline document (CTG) for VOC emissions from wood furniture coating operations. The CTG will be used by States to develop wood furniture coating regulations. The EPA is also developing a national emission standard for hazardous air pollutants (NESHAP) for wood furniture manufacturing. Midwest Research Institute is helping the EPA develop both the wood furniture CTG and the NESHAP. The use of regulatory negotiation, a type of consensus-building process, has been initiated for both the wood furniture CTG and the NESHAP.

As part of the CTG project, a cost analysis of VOC reduction alternatives was performed. This paper describes the analysis used to examine the cost to the wood furniture industry associated with adopting coatings which release less VOC.

INTRODUCTION

The purpose of this paper is to demonstrate the methodology that can be used to estimate the costs and emission reduction associated with using lower-VOC coatings. The costs of switching to lower-VOC coatings are site-specific, and the costs presented here should be viewed accordingly. This paper discusses the initial cost analysis that was performed for the wood furniture CTG project. The CTG project and the cost analysis are described in the draft CTG. The original analysis has since been expanded and revised based on comments and information received from the industry. These revisions have not been finalized and therefore are not discussed quantitatively here. Because the CTG is currently the subject of a regulatory negotiation process, the methodology may change before the CTG is complete.

The cost analysis performed for the CTG evaluated two primary VOC control strategies - the use of add-on controls (with and without exhaust-flow reduction techniques) and the use of lower-VOC coatings. Only the lower-VOC coatings cost analysis is discussed in this paper.

The control techniques guideline will define reasonably available control technology (RACT). RACT applies to existing facilities. Therefore, the cost analysis discussed in this paper evaluated the costs of retrofitting an existing facility to switch from conventional solventborne coatings to lower-VOC coatings.

The objective of the analysis discussed here was to develop the costs and VOC emission reductions associated with a variety of VOC control strategies. These costs and emission reductions were then used to calculate the "cost effectiveness" of the various control strategies, i.e., the cost per unit of VOC reduced (\$/ton VOC reduced). The calculated cost effectiveness data were used in conjunction with other information to evaluate the various control strategies during development of the draft CTG. This paper focuses only on the development of the cost effectiveness data.

INDUSTRY AND COATING INFORMATION

The wood furniture industry was characterized, and the feasibility of a variety of lower-VOC coatings was evaluated. In this section, the finishing process is described, the characterization of the industry by model plants is discussed, and the lower-VOC coatings evaluated are presented.

Finishing Process

The finishing process varies with the industry segment and the facility. Residential furniture manufacturers generally assemble their pieces and then finish them. The remainder of the industry also prefinishes some unassembled pieces. The coatings used in the wood furniture industry include but are not limited to stains, sealers, and topcoats. Coatings are usually spray-applied, although flatline coating methods such as curtain coating and rollcoating are used as well. The residential furniture manufacturing industry generally uses manual spraying, whereas the rest of the industry uses both manual and automatic spraying.

The finishing process may be a single step or multistep operation. The coating may be manually or automatically spray-applied in the spray booth. The piece then leaves the booth and may be wiped before entering the flash area, where the faster solvents are allowed to evaporate. Depending on the number of steps in the finishing sequence, the piece may then enter an oven and, after cooling, may be sanded, after which subsequent coatings may be applied.

Model Plants

A cost analysis for an individual facility would use facility-specific information that presumably would be readily available. The cost analysis described here was performed for the entire wood furniture coating industry. Therefore, "model plants" were developed to represent the wood furniture coating industry. The model plants were developed based on information supplied by wood furniture manufacturers, coating suppliers, application equipment suppliers, and industry representatives.

In developing model plants, the industry was broken down into two main groups: residential furniture manufacturers and "other." Included in the "other" category are cabinet manufacturers, office and institutional furniture manufacturers, and store fixture manufacturers.

The "other" category uses a finishing sequence that consists basically of applications of stain, sealer, and topcoat. Residential furniture manufacturers using a short finishing sequence use essentially the same sequence, except they also apply a washcoat after the stain, before the sealer. Residential furniture manufacturers using a long finishing sequence use the same coatings as manufacturers using a short sequence, but the coatings are applied more frequently and additional coatings, including filler, wiping stain, and highlight, may also be used.

For purposes of the analysis, the size of the model plants was based on total annual VOC emissions. Total VOC emissions of 225 tons per year (tons/yr) corresponds to the medium model plant, and 500 tons/yr corresponds to the large model plant. The smaller model plants were subdivided into three categories with the following emission cutoffs: extremely small - 10 tons/yr, very small - 35 tons/yr, and small - 50 tons/yr. The very small model plant cutoff has since been revised from 35 to 25 tons/year.

The subdivision of model plants is shown in Figure 1. For model plant purposes, the residential furniture manufacturing segment, which primarily uses solventborne nitrocellulose lacquer coatings, was further segregated by short and long finishing sequence, and then by size. The majority of the "other" category primarily uses acid-catalyzed solventborne coatings and generally one basic finishing sequence. The "other" industry segment was broken down by manual and automatic spraying, and then by size. Due to the capital investment required for an automatic spray application system, it was assumed that small facilities would not use automatic spraying.

Lower-VOC Coatings Evaluated

The first step of the life cycle analysis involved determining which lower-VOC coatings are technically feasible for the wood furniture coating industry. A detailed description of the lower-VOC coatings available to the wood furniture industry is not provided here but can be found in the draft CTG. Initially three primary lower-VOC coating types were identified as technically feasible for at least some segments of the wood furniture coating industry: waterborne, polyester, and polyurethane. (The UNICARB® coating system was evaluated later and this analysis is discussed under the section titled "Additional Costs Evaluated"). Polyester and polyurethane coatings are similar in terms of VOC content, solids content, and price. Therefore, in the cost analysis, polyester and polyurethane coatings were treated as a single category, referred to as polyester/polyurethane (pe/pu) coatings. Waterborne coatings can be used exclusively or in conjunction with conventional solventborne coatings. Similarly, pe/pu coatings can be used in conjunction with either conventional solventborne or waterborne coatings, or some combination thereof.

A total of five lower-VOC coating control strategies were originally evaluated: full waterborne, hybrid waterborne, pe/pu, hybrid pe/pu, and hybrid waterborne in conjunction with add-on controls. A full waterborne coating system, consisting of all waterborne coatings, was evaluated. A full waterborne coating system was considered technically feasible for all the model plants except the residential furniture manufacturers using a long finishing sequence. A hybrid-waterborne coating system, consisting basically of waterborne sealer and topcoat in conjunction with other conventional solventborne coatings, was considered technically feasible for all of the model plants. A pe/pu system, consisting of pe/pu sealer and topcoat, in conjunction with conventional solventborne coatings, was evaluated. A hybrid pe/pu coating system, basically consisting of pe/pu sealer and topcoat in conjunction with both waterborne and conventional solventborne coatings, was also evaluated. The pe/pu and hybrid pe/pu coating systems were considered technically feasible for all of the model plants. The use of a hybrid waterborne coating system in conjunction with add-on controls controlling VOC emissions from the solventborne coating steps was evaluated but like the other add-on control analyses, will not be discussed here.

REDUCTION IN VOC EMISSIONS

The thickness of a coating, once applied, is referred to as the coating "build." The build is a function of the amount of solids applied. For all of the coating steps except stains, washcoats, and highlights, it was assumed that the amount of coating used is a function of the final coating thickness the user wants to apply to the piece. Thus, it was assumed that the total amount of solids applied would be independent of the coating used. The solids content of lower-VOC coatings is generally higher than that of conventional coatings. For the coatings for which build is important, this translates into decreased coating usage. The amount of lower-VOC

Figure 1. Model plants for the wood furniture CTG.

coating required was calculated by multiplying the amount of conventional coating required by the ratio of the solids content of the lower-VOC coating to that of the conventional coating.

For some very low-solids coatings such as stains, washcoats, and "highlights," color penetration, rather than build, is of primary importance. Waterborne stains, washcoats, and highlights are formulated such that the coverage on a per-gallon basis is the same as their solventborne counterparts. Therefore, it was assumed that the same quantity of these reformulated materials is required as of their solventborne counterparts.

The VOC content of the reformulated coatings evaluated is generally lower than that of conventional solventborne coatings. Thus, for every gallon of reformulated coating used, less VOC is emitted. Using the VOC content and the quantity of conventional coating used and the VOC content and usage of the reformulated coating, the emission reduction was calculated for each reformulated coating step. The approximate VOC emission reductions associated with each of the reformulated coating systems that were evaluated are shown in Table 1. In calculating VOC emissions from all coatings, it was assumed that all of the VOC contained in the coating is emitted.

TABLE 1. REFORMULATED COATING SYSTEMS, REDUCTIONS IN EMISSIONS BY INDUSTRY SEGMENT, PERCENT

Model plants	Residential furniture short finishing sequence	Residential furniture long finishing sequence	"Other" industry
Waterborne system	88	N/Aª	80
Hybrid waterborne system	59	54	55
Polyester/polyurethane system	55	50	50
Hybrid polyester/ polyurethane system	84	51	75

^aNot applicable.

COSTS ASSOCIATED WITH LOWER-VOC COATING SYSTEMS

The variety of costs that may be associated with switching from a conventional solventborne coating system to a lower-VOC coating system are shown in Figure 2. These costs may include incremental coating costs, the cost of increased material storage requirements, the need for additional drying capability, modifications to the existing coating supply and application system, and the need for a clean room environment. The costs that will be incurred when switching from a conventional to a lower-VOC coating system depend on the existing facility and the type of lower-VOC coating system used. Each of these costs is discussed below, and the methodology used to estimate the costs is described.

Coating Cost

Lower-VOC coatings are usually more expensive on a per-gallon basis than conventional solventborne coatings. However, as discussed above, fewer gallons of many of the lower-VOC coatings are used, due to the increased solids content. Therefore, there may be an incremental coating cost or savings associated with using lower VOC coatings. The cost of using both conventional and lower-VOC coatings is calculated by multiplying the per-gallon cost by the total number of gallons of coating used. The difference between these costs represents the incremental coating cost. The incremental coating cost of waterborne and hybrid waterborne coating systems represents from approximately 65 to 90 percent of the total annualized costs of switching. Incremental coating costs only represent from 1 to 36 percent of the total annualized costs for pe/pu coating systems, and from 1 to 60 percent for hybrid pe/pu systems.

COSTS OF SWITCHING

- Coating cost
- Material storage
- Additional drying capability
- Coating circulation/application system modifications
- Clean room
- Operating costs
- Other costs

Material Storage

In medium and large wood furniture coating facilities, conventional solventborne sealers and topcoats are usually stored in large bulk tanks located outside the building. The other coatings are usually stored in 55-gallon drums or other containers inside the building in heated storage areas. In small plants, all coatings are usually stored inside in containers in heated storage areas. If a facility were to switch to waterborne or pe/pu sealers and topcoats, the reformulated sealers and topcoats would have to be stored indoors, so increased indoor heated storage would be required.

The amount of indoor storage required was calculated assuming all coatings are supplied in 55-gallon drums. It was assumed that due to land constraints, the coating storage building would be beside the existing building. Waterborne coatings usually contain some solvent, and pe/pu coatings may contain solvent that becomes part of the final film. Coatings that contain solvent may have to be stored in a 2-hour fire-rated building if the building is beside the main facility. Therefore, assuming the new storage area would be right next to the existing building is a conservative assumption. In calculating the amount of storage space needed, the reformulated sealer and topcoat coating usage was first calculated. Then using the calculated reformulated coating usage, the turnover rate was increased from once every 3 months to once per month. The storage space requirements were calculated based on 20 percent excess capacity to provide for increased production. The installed capital cost of a 2-hour fire-rated building averaged around \$380 per 55-gallon drum stored, based on 4 square feet per drum. It was assumed that the existing bulk material storage tanks would be left in place with no additional expense.

Additional Drying Capability

Some of the reformulated coating systems may require additional drying capability. How this need is addressed depends on the existing facility, the configuration and speed of the finishing line, the substrate being finished, and potentially many other factors. In some facilities, the need for increased drying capability may be addressed by simply slowing down the line (or increasing the amount of time allowed for drying in a facility without a finishing line). In other facilities, upgrading existing ovens may be sufficient, whereas in still other facilities additional ovens may be needed. For purposes of our analysis, it was assumed that the additional drying capability requirement would be provided by adding high-airflow convection ovens to the existing line. It was assumed that space for the new ovens was available or could be made available at minimal expense.

The number of ovens needed varies depending on the size of the model plant, the type of reformulated coating system being used, and the number of existing conventional ovens. For the waterborne coating systems, it was assumed that a preheater oven is needed before any coatings are applied and that an oven is required after each waterborne coating is applied. It was assumed that the pe/pu coatings cure via a catalytic reaction with the curing time reduced by means of an oven. Therefore, an oven is needed after each pe/pu coating is applied.

Based on information provided by oven suppliers, it was conservatively estimated that a new 20-foot long high-airflow convection oven would cost \$48,600 installed. In addition to the cost of the ovens, there are increased electrical and fuel requirements associated with operating the new ovens. These costs are discussed later with other additional operating costs associated with the use of lower-VOC coatings.

Coating Circulation/Application System Modification

If a facility switches from conventional solventborne coatings to waterborne coatings, some modifications to the coating circulation and application system will be required. Modifications may have to be made to the coating circulation system as well as to the supply lines from the mix room to the spray booths and the application system. The cost to retrofit a facility with an appropriate paint circulation system so that waterborne coatings can be used is a function of the location of the central mix room relative to the spray booths (if a central mix room exists), the number of spray booths, and the number of mix tanks feeding the spray booths.

It was assumed that in a small facility there is no central mix room and that the coating materials are pumped directly from a drum, located at the spray booth, to the spray gun. For small model plants a modular paint delivery system is used to transfer coatings from the drum to the spray gun. A modular system consists of a coating storage drum, the drum cover and assembly, fluid regulators, valves, pumps, hoses, and a spray gun.

If waterborne coatings are used, all components of the modular system would have to be made of stainless steel. Based on vendor information, a cost of \$9,100 per modular spray unit was estimated.

For medium and large facilities, it was assumed that a new stainless steel paint circulation system would be needed if waterborne coatings were used. Modifications to the material transfer lines would be needed, as well as changes in the mix room and the spray booths. The replacement stainless steel systems were assumed to be constantly recirculating systems. The constant circulation of waterborne coatings is necessary to avoid agglomeration of the coating material in the supply lines. The material transfer lines circulating coatings between the mix room and the spray booths would have to be made of stainless steel. It was assumed for the purposes of the analysis that new stainless steel transfer lines would be needed at all facilities. Based on information supplied by wood furniture industry representatives, 200 feet of coating transfer line is needed for each spray booth. The 200 feet includes 100 feet from the mix room to the booth plus 100 feet of return line. Based on vendor information, stainless steel pipe (304 grade or better) suitable for the transfer of coatings costs \$20 per foot of pipe, installed.

For waterborne coatings, changes in the mix room will be required to accommodate coating storage, to agitate the coating material, and to pump and regulate the coating materials. Based on vendor information, the installed capital cost of a mix tank was estimated as \$25,600. The total installed capital cost of the mix tank assembly (pumps, agitator, valves, regulator, and hoses) was estimated as \$8,800.

Modifications would also be needed at the spray booths in medium and large facilities that switch to waterborne coatings. The spray booth equipment would have to be stainless steel capable of handling waterborne coatings; the required new equipment at each booth would include fluid valves, a regulator, a fluid hose to the gun, an air hose, a paint heater, a spray gun, and an oil/water separator for the air supply. Based on vendor information, it was estimated that the equipment described above would cost \$1,400, not including the cost of the paint heater. The paint heater would be supplied separately at a cost of \$1,850. The above equipment would be needed at each spray booth.

Clean Room

According to coating suppliers, polyester and polyurethane coatings are very difficult to repair after curing. If dirt gets on the coated piece before it is fully cured, it cannot be removed by conventional means such as rubbing and polishing. Therefore, to minimize the number of rejects that cannot be repaired, the pe/pu coatings should not be exposed to dirt and should be applied in a clean room environment. A clean room is maintained at a positive pressure to prevent dirt from entering, and all air entering the room is filtered. The entire finishing room may function as a clean room, or the clean room may be a tunnel encompassing the booth/flash/oven area. For the purposes of this analysis, it was assumed that the clean room would be in the form of a tunnel encompassing the sealer and topcoat spray booth/flash/oven areas.

The size of a clean room is a function of the dimensions of the finishing line and the total exhaust rate from the clean room tunnel. The cost of a clean room tunnel is very facility-specific and difficult to assess for each of the broad model plant categories. Two clean room vendors were contacted, but only one supplied the estimated cost of installing a clean room in an existing furniture coating facility. An approximate cost of \$1 million per clean room was provided by one vendor. It was assumed that if pe/pu coatings are used, one clean room tunnel would be required for each finishing line within the facility. Due to the facility-specific nature of clean rooms and the single cost estimate, there is less confidence in this estimate than in those associated with other costs for switching to lower-VOC coatings.

Additional Costs Evaluated

Estimates of several additional costs have been made since the publication of the draft CTG. Additional operating costs, the cost of using a UNICARB® coating system, and the costs of a flatline coating operation switching to lower-VOC coatings were estimated and are described below.

Operating Costs. Additional operating costs associated with switching to lower-VOC coatings include the cost of fuel and electricity required for the new ovens, the incremental waste coating disposal cost, and taxes, insurance, and administrative expenses.

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Increased fuel and electricity costs associated with the additional ovens are operating costs associated with the use of some lower-VOC coatings. The fuel provides the heat, and the electricity is needed for the fans. Based on information obtained from furniture and oven manufacturers, the per-oven natural gas requirements were estimated to be 700 million British thermal units per year.^{2,3} Oven manufacturers indicated that a typical oven used in the wood furniture industry requires about 12 kilowatts of electricity to operate.^{2,4} These fuel and electricity requirements translate into an operating cost of approximately \$3,470 per oven annually.

Based on information supplied by wood furniture manufacturing industry representatives, it was assumed that the volume of waste coating produced is about 5 percent of total coating use. Because the heating value of conventional solventborne coatings is relatively high, the disposal cost is relatively low (about \$0.70/gallon of waste coating). Because the heating value of waterborne coatings is relatively low, the disposal cost is relatively high (about \$3.50/gallon of waste coating). Therefore, when a facility switches to waterborne coatings, though the total volume of waste coating is less because fewer gallons of coatings are used, the overall waste coating disposal cost may increase. It was assumed that there is no incremental waste coating disposal cost associated with the use of pe/pu coatings.

Indirect annual costs are an operating cost associated with the purchase of any equipment.

Administrative expenses were estimated as 2 percent of the total capital investment, and insurance and property taxes were both estimated to be 1 percent of the total capital investment.

Cost of the UNICARB® Coating System. When the original cost analysis was performed, the UNICARB® coating system was not being used in production in any wood furniture manufacturing facility. Because it has since been used in production in several wood furniture coating operations, the costs and VOC emission reduction associated with the UNICARB® system have been estimated. The UNICARB® system evaluated consists of reformulated sealer and topcoat being used with conventional coatings. The UNICARB® system can also be used in conjunction with waterborne coatings, although this option was not evaluated.

The UNICARB® system uses CO₂ to replace some of the solvent in the coatings. UNICARB® coatings are formulated only with coalescing solvents, diluent solvents are left out. Coalescing solvents are slow evaporating, fluent solvents are fast evaporating. The highly viscous coating and supercritical CO₂ are mixed in a chamber and released as atomized paint through a spray gun. The CO₂ evaporates from the paint particles before they contact the product being coated. The deposited paint containing the coalescing solvents cures in the conventional way.

There is a reduction of VOC emissions associated with the use of UNICARB® coatings. The reduction in VOC emissions results from the lower VOC content of the UNICARB® coatings and the higher solids contents of the coatings, similar to the waterborne coatings. The major costs associated with switching from conventional solventborne coatings to a UNICARB® coating system include the incremental cost of the coatings, royalty costs, the need for additional drying capability, the UNICARB® spray system, CO₂ and tank rental, and CO₂ storage. The methodologies used to estimate these costs are described below.

Because acid-catalyzed UNICARB® coatings have not been developed and UNICARB® spray equipment as presently designed cannot spray two-component coatings, it was assumed that UNICARB® coatings are not presently feasible for the "other" industry segment using acid-catalyzed coatings. For residential furniture manufacturers, the UNICARB® coating system consists of UNICARB® sealer and topcoat with conventional nitrocellulose coatings for the remaining coating steps.

The incremental coating cost associated with using UNICARB® coatings was calculated in the same way as that for waterborne coatings. Generally less of the UNICARB® coatings are required because of the higher solids content; however, they are generally more expensive on a dollar-per-gallon basis. Incremental coating costs represent from 13 to 50 percent of the annualized costs of switching to the UNICARB® system. The reduction in VOC emissions for UNICARB® coatings was also calculated as it was for the waterborne coatings, as previously described. The emission reduction associated with the use of UNICARB® coatings varies from about 35 to 40 percent.

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There is a \$2/gallon royalty charged by Union Carbide, the developer of the UNICARB® system. The user must pay Union Carbide \$2 for every gallon of UNICARB® coating sprayed.

In reformulating conventional nitrocellulose coatings to make UNICARB® coatings, the faster solvents are replaced with supercritical CO₂. Although UNICARB® coating manufacturers have attempted to minimize the drying time required with UNICARB® coatings, additional drying time and/or airflow is still required in some instances. Therefore, it was assumed that an oven is needed after each UNICARB® coating is applied. The capital and operating costs associated with the additional ovens were estimated as described previously for waterborne coatings.

The UNICARB® coatings require a specialized spray application system to apply the coatings. At present, Nordson Corporation is the only application equipment vendor that is manufacturing the UNICARB® spray application systems. According to information supplied by Nordson in 1992, a typical 0.4-gallon-perminute unit designed for the wood furniture industry costs \$35,000. This cost applies to a predesigned unit, with one spray gun. Each additional gun costs about \$625.8 Installation costs depend on the distance to the CO₂ source and the coating material supply source but typically costs around \$4,500.7,8

A single UNICARB® spray application system can supply multiple spray guns. The number of guns is theoretically limited only by the maximum possible flowrate of the unit; Nordson Corporation has found that about four guns is the practical limit. Sealer and topcoat cannot be sprayed from the same unit. The furniture industry often uses multiple sheens of topcoat, and Nordson Corporation has designed and tested a unit that can spray multiple sheens of topcoat. The additional manifolds and reservoirs needed to spray four different sheens adds \$10,950 to the cost of the unit; each additional sheen costs \$2,000.8

In developing the costs for the model plants, it was assumed that regular UNICARB[®] units are used to spray sealer, and multisheen units are used to apply topcoat. The number of units required was determined by the finishing sequence and the number of finishing lines. For each model plant, it was estimated that one additional multisheen unit would be purchased as backup.

As previously mentioned, CO₂ is required when using UNICARB[®] coatings. Based on information provided by the UNICARB[®] equipment manufacturer, the cost of CO₂ tank rental plus the cost of the CO₂ was \$1.17/gallon of coating sprayed. In most instances, the CO₂ is stored in bulk storage tanks. It was assumed that a storage building would be required for CO₂ storage and that the storage building would cost \$15,000.

Operating costs associated with the purchase and use of a UNICARB® coating system include the cost of fuel and electricity for the new ovens, and taxes, insurance, and administrative costs. These operating costs were estimated for the UNICARB® system using the same methodology as that described earlier for the waterborne and pe/pu coating systems. It was assumed that there is no incremental waste coating disposal cost associated with UNICARB® coatings.

Flatline Coating Operations. Some percentage of the furniture manufacturing facilities presently use flatline coating operations to apply some or all of the coatings. Some additional percentage of the industry spray-finishes flat components and then assembles the components. In many instances, these operations could also use flatline finishing methods. The methodology that could be used to estimate the costs is presented, but due to the preliminary nature of the estimates, the results are not presented.

If an existing flatline coating operation were to switch from conventional solventborne coatings to lower-VOC coatings, the VOC emission reduction would be associated with the decrease in usage associated with the higher solids content and the lower-VOC content of the lower-VOC coatings. The costs associated with such a switch would include the incremental cost of the coatings and other operating costs (oven electricity and fuel requirements, incremental waste disposal costs, and taxes, insurance, and administrative expenses).

If an existing spray operation using conventional solventborne coatings was to become a flatline coating operation using lower-VOC coatings, the total coating usage would decrease for two reasons: the increased solids content of the lower-VOC coatings and the increased transfer efficiency associated with flatline

application compared to that of spray application. The costs of such a changeover would include the incremental coating cost (or savings), the cost of the flatline coater, the cost of removing the old line, the capital and operating costs of additional ovens, the incremental cost of waste coating disposal, and taxes, insurance, and administrative expenses.

OTHER CONSIDERATIONS

There are other factors to consider in converting a facility from a conventional solventborne system to pe/pu coating system, a waterborne coating system, or a UNICARB® coating system. These factors are discussed here, but costs associated with these factors have not been assessed in this cost analysis because of their facility-specific nature.

The first factor regards physical modifications that a plant must undergo to accommodate pe/pu coating systems. If a facility were to convert some or all of its coating steps to a pe/pu coating system, the facility would probably remove the existing finishing line (or a portion of it) and replace it with a new line housed in a clean room environment. This differs from the conversion to a waterborne coating system in which the facility would most likely retrofit the existing line(s). The cost for a facility to remove an existing finishing line may be significant but is not incorporated into the total installed cost of \$1 million for a clean room tunnel. Also, it was assumed that the pe/pu coatings are two-component catalyzed coatings. \$10,11\$ Catalyzed pe/pu coatings must be applied using two-pack spray application equipment. The catalyst must be measured (weighed) prior to mixing and an exact amount of catalyst is required. The cost analysis in this chapter does not account for the replacement of existing spray equipment with the two-pack spray equipment, neither does it incorporate the cost of scales for weighing the catalyst and the cost to train workers to perform such a task. Also, the short pot-life of the pe/pu coatings may result in a cost to the plant in terms of more waste, but this cost is not accounted for in this analysis.

Another factor to consider in converting from conventional solventborne coatings to a reformulated coating system is costs associated with downtime. Whenever a new coating system is installed, there is downtime associated with the installation and training of the workers. These costs have not been assessed. One final consideration in implementing a pe/pu coating system is the toxicity of the coating materials. Air purifying respirators and, in some instances, supplied air respirators are required when applying pe/pu coatings.⁶⁷ The cost analysis in this chapter does not account for the cost of this equipment, the cost to train workers to operate while wearing this equipment, or the cost of lost production, if any, due to the decreased mobility of the worker.

Several potential savings were also not quantified due to their facility-specific nature and the difficulty of quantifying the monetary value of reduced employee exposure. Savings may result from switching from solventborne to lower-VOC coatings due to decreased worker exposure. The reduced exposure to solvents may result in a health benefit to the workers, which could conceivably result in decreased worker absenteeism. However, it is difficult to accurately quantify the monetary value of decreased worker exposure or any decrease in absenteeism that may result.

Savings may result from decreased insurance premiums if a facility switches from solventborne coatings. However, a Factory Mutual representative said that insurance premiums would not automatically reduce if a facility switched to waterborne coatings. The representative indicated that decisions regarding premiums are site-specific, and an analysis of an entire facility would be required. ¹⁴

CONCLUSIONS - COMPARISON OF REFORMULATED COATING SYSTEM TOTAL COSTS

Because the final wood furniture CTG is currently involved in a regulatory negotiation process, and the model plants and associated costs may change as a result of that process, the individual model plant costs that were developed as a result of the first cost analysis will not be discussed specifically. Instead, the relative cost effectiveness of the various lower-VOC-coating alternatives evaluated are discussed.

The cost effectiveness of the five lower-VOC coating systems evaluated is presented in Figure 3. Generally, the analysis indicated that for the model plants evaluated, hybrid waterborne is the most cost-effective lower-VOC coating system alternative, with cost effectivenesses ranging from around \$1,300/ton to

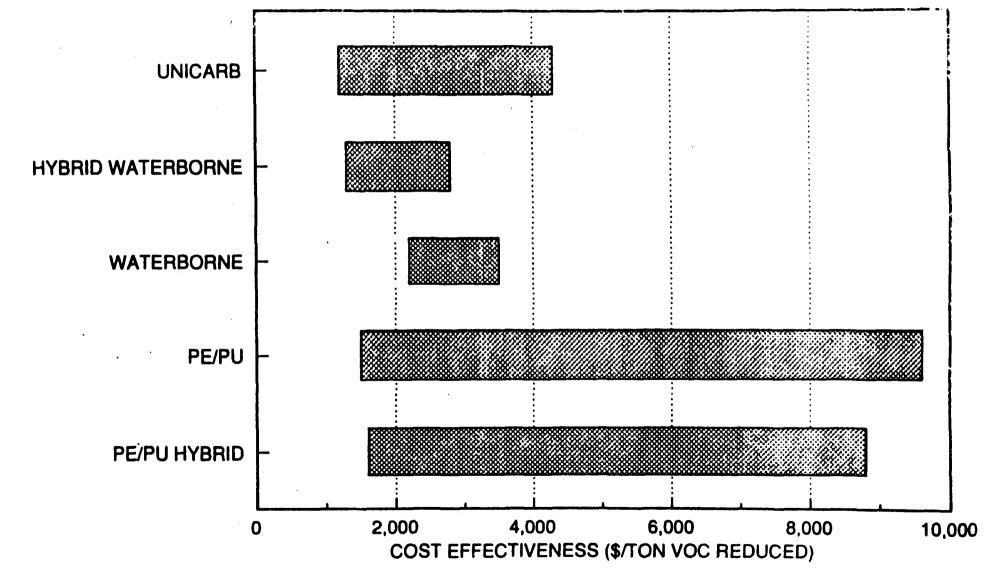


Figure 3. Cost effectiveness of lower-VOC coating systems.

\$2,800/ton of VOC reduced. The UNICARB® coating system's cost effectiveness ranges from around \$1,200/ton to \$4,300/ton of VOC reduced. The cost effectiveness of waterborne coating systems ranged from about \$2,200/ton to \$3,500/ton of VOC reduced. The cost effectiveness of pe/pu and hybrid-pe/pu coating systems is considerably higher in most instances (up to around \$9,600/ton).

Caution should be used in evaluating the cost effectiveness of the pe/pu and hybrid pe/pu systems. The lower cost effectiveness estimates for these systems correspond to the residential furniture (long finishing sequence) and "other" (automatic spraying) model plants. Uncertainty in the estimate of clean room costs and the flowrates associated with automatic spraying operations results in uncertainty in the cost effectiveness estimates for these model plants. The actual cost effectiveness estimates for these model plants may be higher.

The UNICARB® coating system is presently not feasible for the "other" category, which generally uses acid-catalyzed coatings. The cost effectiveness of the other four lower-VOC coating systems evaluated is generally higher for the "other" industry than for the residential furniture industry. That is, it is generally more expensive to reduce a ton of VOCs emitted for the "other" industry than it is to reduce a ton of VOCs for the residential furniture industry. The coatings used today by the "other" industry segment are higher in solids than those used by the residential furniture industry. Therefore, the decrease in coating usage associated with switching to a lower-VOC coating is less for the "other" industry than for the residential furniture industry. This relatively small decrease in coating usage for the "other" industry translates into a higher cost per ton of VOC reduced.

The costs and emission reductions presented in this paper were developed based on the best information available at the time. The purpose of the paper is to demonstrate the methodologies that can be used to estimate the costs and emission reductions associated with using lower-VOC coatings. As the regulatory negotiation process progresses, and more information becomes available, the estimated costs may change.

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DEVELOPMENT OF ULTRA-LOW VOC WOOD FURNITURE COATINGS

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ABSTRACT '

It is estimated that the annual U.S. market for wood coatings is approximately 240,000 m³ (63 million gallons). On this basis, between 57 and 91 million kilograms (125-200 million pounds) of volatile organic compounds (VOCs) are emitted into the air each year from the use of presently used water-borne and solvent-borne systems. The use of "VOC-free" formulations where possible would reduce such air pollution while providing new markets for industries.

Adhesive Coatings Company (ADCO), a small firm specializing in low VOC, two-component, water-based epoxy coatings, holds patents on some of these formulations. Polymer composition variations of the basic epoxy polymer in combination with each of several curing agents were prepared. The resulting emulsions were analyzed through laboratory tests to measure gloss value, drying time, hardness/flexibility, level of solvents, and chemical and stain resistance.

The new formulations contain < 10 g/l (0.1 lb/gal) VOCs which means that these coatings emit practically no VOCs. The physical properties in the can, as applied, and as the cured finish are discussed.

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1.0 INTRODUCTION

It is estimated that the annual U.S. market for wood coatings is approximately 240,000 m³ (63 million gallons). On this basis, between 57 and 91 million kilograms (125-200 million pounds) of volatile organic compounds (VOCs) are emitted into the air each year from the use of presently used water-borne and solvent-borne systems. The use of "VOC-free" formulations where possible would reduce such air pollution while providing new markets for industries.

The South Coast Air Quality Management District (SCAQMD) Rules 1104 and 1136 - Wood Products Coatings require reduction of VOCs from such sources. It is estimated that SCAQMD-wide compliance with these rules would reduce VOC emissions by about 18 Mg (20 tons) per day through a gradual shift from high to low VOC coatings. By phasing in low VOC coatings, instead of requiring installation of add-on controls, SCAQMD believes that furniture manufacturers will be able to comply with SCAQMD's rules without increased costs. To remain competitive in the regulated South Coast Air Basin, coatings formulators and furniture manufacturers have expressed interest in seeing further developments in low

VOC coatings technology.

Adhesive Coatings Co. (ADCO), a small firm specializing in development and commercialization of low VOC, two-component, water-based epoxy coatings, is currently developing coatings which will comply and/or exceed the emissions standards set forth in Rules 1104 and 1136. ADCO currently holds patents on some of these formulations. It is estimated that new formulations of these two component water-based epoxy coatings have the potential to achieve a significant share or complete replacement of the current organic solvent-based coatings. The new formulations contain < 10 g/l (0.1 lb/gal) VOCs which means that these coatings emit practically no VOCs.

Several large companies that manufacture and supply products used in the wood coatings industry have been contacted. The product marketing discussions have centered on how best to commercialize specific ultra-low VOC finished coating applications. Discussions already are underway with two major corporations, both of which are worldwide suppliers of industrial products and services to the coatings, adhesives, and polymer industry and recognized as leaders in providing coatings and ancillary products for the wood industry.

Project Participants:

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2.0 OBJECTIVES

The objective of this project is to develop new low/no VOC wood coatings through continuing research, formulation adjustments, and application testing. In addition to the basic development of the coatings, a marketing plan will be developed to get the products of this project into the public's use.

Efforts are dedicated to conduct joint research into new promising technologies that are sufficiently mature for demonstration to wood product manufacturers. The high value added coating products are developed utilizing existing technical know-how, data, and patents

related to the new technologies.

3.0 PROJECT DESCRIPTION

This new wood coating system consists of an epoxy component (Part A) and an amine curing component (Part B). The complete absence of organic solvents means that this new coating system is not only less hazardous to use but emits practically no VOCs and therefore does not significantly contribute to air pollution. The ultra low VOC content of these new wood coatings was confirmed by tests at the Center for Emissions Research & Analysis (the Center) (see Table A). This new two component water-based epoxy wood coating system has the potential to set a new standard and therefore replace a very significant share of current organic solvent systems in use.

3.1 Coating Characteristics:

This new ultra-low VOC wood coating system is a high performance, two-part, chemically cured, water reducible, fast drying, epoxy product used as a wood coating. It is a hard, durable primer coating that can be applied to a variety of wood surfaces. The coating system, as it now stands, has the following performance properties:

- (a) Less than 10 g/1 (0.1 lb/gal) VOCs,
- (b) Liquid with rapid initial drying characteristics upon application,
- (c) Hardness.
- (d) Flexibility,
- (e) Chemical resistance,
- (f) Effort still required to improve sandability, and
- (g) Effort still required to lessen wood discolorization.

3.2 Technical Approach:

The coating development steps are to make the necessary formulation adjustments, continue with application testing to improve the product characteristics, and overcome the shortcomings. The goal of the project is to develop a wood coating system that will set new industry standards for VOC levels.

The results of the research procedures and laboratory tests are documented and written status reports are prepared detailing the work completed to date along with the identification of areas that may require further investigation.

The technical approach has centered around the following activities:

- 1. Work towards reformulating ADCO's patented epoxy polymer in combination with different curing agents.
- 2. Identify those compositions that yield the best overall coating performance in terms of gloss value, drying time, hardness/flexibility, and chemical and stain resistance.
- 3. Conduct the emission tests required to determine whether the compositions selected have less than 10 g/l VOCs.
- 4. Formulate emulsions with white pigment for those compositions that meet the performance criteria and emissions limits.
- 5. Identify those pigmentations that yield the best overall coating performance in terms of gloss value, drying time, hardness/flexibility, and chemical and stain resistance.
- 6. Conduct the emission tests required to determine whether the pigmentations selected have less than 20 g/l VOCs.
- 7. Prepare different finished wood panel coupons, both clear and pigmented, to demonstrate finished coatings that meet the performance criteria and emissions limits.
- 8. Assess the market acceptance by a written survey and develop two annual marketing reports to summarize the survey results, manufacturer acceptance, cost benefits, and any application limitations.

3.3 Task Description:

The program for making formulation adjustments and undertaking the necessary application testing to meet the desired product characteristic goals are outlined in the following tasks:

Task 1 - Formulation variations

Polymer composition variations of the basic epoxy polymer in combination with each of several curing agents were conducted. The resulting emulsion was analyzed through laboratory tests to measure gloss value, drying time, hardness/flexibility, level of solvents, and chemical and stain resistance. All test results were documented.

Product coating characteristic criteria used in this project included but are not limited to:

- 1. The product will contain VOCs < 20 g/l.
- 2. The product will have a gloss value in the 90-100 range as measured on an 80 degree gloss meter.
- 3. The product will "dry to the touch" in 10 minutes or less and "dry to handle" in 15 minutes or less for temperatures in the range of 45 to 60°C with a relative humidity not to exceed 80%.
- 4. The product will have a demonstrated pencil hardness of at least 2H.
- 5. The product will have a demonstrated chemical, water stain, and chip resistance comparable to other products for the same general use.

Task 2 - Variations in pigmentation

An emulsion was formulated with white pigment for the best epoxy polymer/curing agent ratios selected in Task 1. Laboratory tests were conducted to measure gloss value, drying time, hardness/flexibility, level of solvents, and chemical and stain resistance. All test results were documented.

Task 3 - Preparation of finished coating samples

The existing two-component spray application system developed by Binks Manufacturing Inc. was modified and the application of the coatings was evaluated to determine if it meets the production requirements of wood furniture manufacturers. The results are shown in Table B.

Task 4 - Market development

Several wood furniture manufacturers and coating suppliers were contacted to identify wood coating concerns, current application methods, costs, and critical areas for product improvements. Marketing information related to the wood coatings market was collected. The market segments in turn are subsegmented into wood furniture, kitchen cabinets, new case goods, plywood (hardboard), regenerated wood products, flat stock finishes, and specialty finishes. This information was reviewed to establish what specific data still need to be collected and how they should be used in structuring the planned market survey of wood coating suppliers.

Two market development reports will be prepared to summarize how the new wood coatings

address the concerns of the marketplace, potential cost benefits, and limitations.

4.0 RESULTS AND FUTURE DEVELOPMENT

Work on variations of the patented epoxy polymer in combination with different curing agents was finalized (see Table C). The synthesis of the resin into a new resin was completed and was followed by the emulsification of the product in water. Analysis was expended by selecting those additional curing agents not previously evaluated but were known to be sufficiently reactive to achieve proper film formation and acceptable properties. Each resulting film is characterized as to its properties (see Table D).

Various formulations of curing agents in combination with the various epoxy polymers were evaluated to precisely identify those combinations that yield the best overall coating performance and meet the desired coating characteristic criteria (see Table D).

Table A. VOC content of wood coatings				
SAMPLE DESCRIBED AS: ADHESIVE COATINGS CO. PART B 65-99 (CLEAR) PART A 76-64 (WHITE)				
SOURCE:	2755 Campus Drive, Suite 125 San Mateo, CA 94403			
ANALYTICAL WORK PERFORMED, ME	THOD OF ANALYSIS, AND RESULTS:			
Volatile content by ASTM-D-2369-81 ¹ , dens 3792 (GC), and calculations by ASTM-D-39	sity by ASTM-D-1475-60, water by ASTM-D-060-81 Section 8.2.4.			
VOCs	content ²			
	coating) = <10 material) = <10			

The Center will also develop a low/no VOC "sanding sealer" wood coating so that a complete

¹ The detection limit for VOCs is 10 g/l.

² The two products (76-64 and 65-99) were mixed 5: 1 prior to actual analysis.

low/no VOC wood coating system will be available for public use. The extra developmental work will be focused on reformulating wood base coatings, determining performance characteristics and conducting application and emission testing for a new fast drying, solvent free wood sanding sealer.

Table B. Physical properties of applied finish		
COLOR	Clear or pigmented white	
SERVICE TEMPERATURE LIMITS	-18 to 120° C (0 to 250° F). May discolor over 60° C (140° F) after a long period of baking	
GLOSS	Clear coating - 90 @ 80° meter Pigmented coating - 75 @ 80° meter	
HARDNESS	Pass 2H pencil	
FLEXIBILITY	Pass 3 mm (1/8 in.) mandrel bend on steel	
IMPACT RESISTANCE	Direct - Pass 3 m/kg (60 in./lb) Indirect - Pass 1.5 m/kg (30 in./lb)	
ADHESION	Pass crosshatch 100%	
STAIN RESISTANCE (After 1 hour of exposure)	Coating is resistant to: Coffee Grape juice Mustard Ketchup Carbonated cola beverage 100 proof vodka Shoe polish Laundry spot cleaner Detergent 1,1,1 trichloroethane Acetone Petroleum solvents Ethyl alcohol	

Cure conditions including curing rate, extended pot-life, and rheology modifications to include use of thickeners in the formulation for adjusting the flow of coatings will be evaluated. Both "clear" and "white" finished wet samples for emission testing will be prepared utilizing a two-component variable ratio spray application gun.

Table C. Physical properties (in the can)		
APPEARANCE	Milky white, single-phase, creamy liquid	
VISCOSITY	Part A: 0.9 Pa.s (900 centipoise) Part B: 0.9 Pa.s	
рН	5.5 to 7.5	
ТҮРЕ	Two components: Part A - Epoxy emulsion Part B - Curing agent	
DENSITY	Clear: 1030 g/l (8.60 lb/gal) White: 1500 g/l (12.5 lb/gal)	
SOLIDS	50% by volume	
FLASH POINT	over 150° C (300° F)	
SHELF LIFE	> 6 months	
VOC CONTENT	< 10.0 g/l (0.1 lb/gal)	

Table D. Application properties			
MIX RATIO	Part A - 5 parts Part B - 1 part		
THINNING SOLVENT	Water		
CLEANUP	Warm soapy water		
FILM THICKNESS	75-125 μm (3.0-5.0 mils) wet 40-65 μm (1.5-2.5 mils) dry		
THEORETICAL COVERAGE	9 m ² /1 (360 ft ² /gal) @ 50 μm (2 mils)		
DRYING TIME @ 50° C	To touch: 10 min To recoat: 20 min Tack free: 15 min Full cure: 60 min		
RECOATABILITY	Very good		

SESSION 9

AEROSPACE APPLICATIONS

PAPERS PRESENTED:

"Replacement of Chromated Epoxy Primers/Wash Primers for Ground Support Equipment and Space-Related Flight Hardware"

by

Mark E. Lindsay

Lockheed Missiles & Space Company, Inc.

Sunnyvale, California

"An Investigation of Flexibility Test Methods for Low-VOC Aerospace Coatings"

by

Angela M. Brown

Boeing Defense & Space Group

Seattle, Washington

"Waterborne Maskant"

bν

Mark D. Jaffari

Malek, Inc.

San Diego, California

"Low-VOC Organic Coatings for Commercial Aircraft Application"

by

T. D. Leland

C. M. Wong

Boeing Commercial Airplane Group Materials and Processes Engineering

Seattle, Washington

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

Replacement of Chromated Epoxy Primers/Wash Primers for Ground Support Equipment and Space Related Flight Hardware

Mark E. Lindsay Lockheed Missiles & Space Company, Inc. P.O. Box 3504 O/78-30, B/564 Sunnyvale, CA 94089-3504

INTRODUCTION

Hexavalent chromium is listed as a hazardous air pollutant (HAP) under Section 112 of the Clean Air Act of 1990. In 1990, Lockheed Missiles and Space Co. (LMSC) took a proactive approach to eliminate/reduce the use of chromate containing compounds. Compounds containing hexavalent chromium are used as corrosion inhibiting pigments in paint primers such as epoxy primers and wash primers.

LMSC uses several epoxy primers and wash primers that contain up to 50% by weight chromated compounds as pigments. The primers primarily serve three functions. They (1) increase the compatibility between the substrate and the topcoat, (2) improve adhesion, and/or (3) improve the corrosion resistance of the substrate. Wash primers are used as a pretreatment for bare steel, copper, nickel, titanium, and aluminum surfaces to promote adhesion prior to priming where an immersion chemical treatment is not feasible. When this study began, eight chromated epoxy primers/wash primers were identified in use at LMSC (see Table I).

TABLE I - LMSC CHROMATED PRIMERS

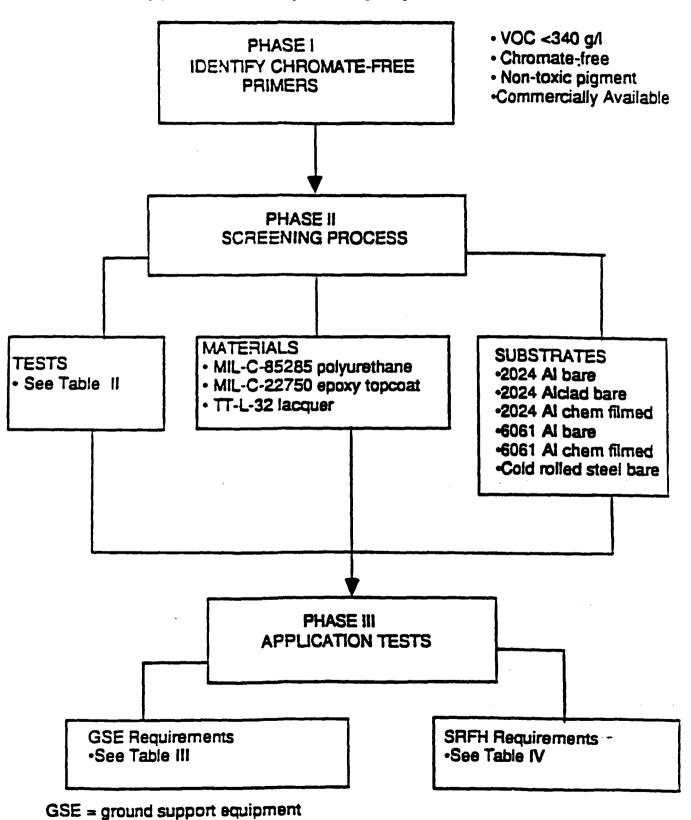
SPECIFICATION	DESCRIPTION	CHROMATE CMPD.	USAGE 1989-90
MIL-P-23377	Epoxy primer	Strontium chromate	75 gal/year
LAC 37-4467	Chemglaze primer	Zinc chromate	48 gal/year
MIL-C-8514	Wash primer	Zinc chromate	8 gal/year
DOD-P-15328	Wash primer	Zinc chromate	Not used in 1990
LAC 37-4850	Zinc chromate primer	Zinc chromate	Not used in 1990
MIL-P-85582	Water reducible primer	Barium/strontium	6 gal/year
TT-P-1757	Zinc chromate primer	Zinc chromate	2 gal/year
LAC 37-4698	Wash primer	Zinc chromate	2 gal/year

APPROACH

Epoxy Primers

The approach for replacing epoxy primers is illustrated in Figure I. Chromate free epoxy primers were evaluated for the two major applications in LMSC's Space Systems Division (SSD); ground support equipment (GSE) and space related flight hardware (SRFH). The approach consists of identifying candidates, screening the candidates and performing additional tests depending on the application (GSE or SRFH). The requirements for the screening tests are presented in Table II and the specific requirements for GSE and SRFH are presented in Tables III and IV, respectively.

Figure I
Approach to Replace Epoxy Primers



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SRFH = space related flight hardware

TABLE II - SCREENING TEST REQUIREMENTS AND METHODS

TEST	REQUIREMENTS	METHODS
Viscosity-initial	Info only	#4 Ford cup
Viscosity-spray	Info only	#4 Ford cup
Outgassing	Collected volatile condensable material: 0.1% max.	ASTM E 595
	Total mass loss: 1.0% max.	ASTM E 595
Dry time	Tack-free: Info only	Visual
	Dry hard: Info only	Visual
Appearance	Smooth and uniform. No runs, sags, orange peel, wrinkling, bumps, fisheyes, pinholes, craters, blisters, grit, or seeds.	Visual
Adhesion	No lifting, peeling, or coating separation	FTMS 141, Method 6301
Lifting	No lifting or film irregularity after 5 hours	Visual
Knife test	No flake, chip, or powder	FTMS 141, Method 6304
Impact resistance	10% min. impact elongation	GE Impact tester
Water resistance	No softening, wrinkling, or blistering	4 days in DI water at 120F
Salt spray resistance	No blistering, lifting, or corrosion	Scribed, 1000 hours in 5% salt fog
Filiform corrosion resistance	0.25" corrosion max. from scribes lines	Scribed, 1000 hours in 80% RH at 40C
Fluid resistance	Lubricating oil: No softening, blistering, or adhesion loss	Immersed for 24 hours at 250F
	Hydraulic oil: No softening, blistering, or adhesion loss	Immersed for 24 hours at 150F
Gloss	30 max.	60 degree gloss meter
Volatile organic content	340 g/l max.	BAAQMD method

Table III - REQUIREMENTS FOR GSE

14510 111 112 40111211121110 1 011 402		
Test	Requirement	
5% salt spray resistance	1000 hours	
Filiform corrosion resistance	1000 hours, 0.25 in max. lifting on scribe line	
Wet tape adhesion	No lifting	
Intercoat adhesion (topcoats: MIL-C-85285, Am-E-Pox Enamel and MIL-C-22750)	No separation	

Table IV - REQUIREMENTS FOR SRFH

Test	Requirement
Dry tape adhesion	No lifting
Intercoat adhesion (topcoats for flight hardware)	No separation
Outgassing	TML: 1.0% max. CVCM: 0.1% max.
Coefficient of thermal expansion (CTE)	similar to current primer (LAC 37-4467 Chemglaze primer)

Wash Primers

Bay Area Air Quality Management District (BAAQMD) regulation changes for wash primer VOC (780 g/l to 420 g/l) in 1991 prompted LMSC to investigate replacement wash primers for GSE. A similar approach to the approach described in Figure 1 for epoxy primers was used to replace wash primers. The requirements for wash primers are listed in Table V.

TABLE V - WASH PRIMER REQUIREMENTS

Test	Requirement	Method	
Dry time	Info only	Visual	
Appearance	Smooth, uniform no runs	Visual	
Wet tape adhesion bare steel and aluminum		FTMS 141, Method 6301	
Compatibility with primers (MIL-P-23377, MIL-P-53030 and MIL-P85382)	No intercoat adhesion loss	Visual	
VOC	420 g/l max.	BAAQMD Method 22 or 23	

RESULTS

Epoxy Primers

<u>Phase I.</u> An industry search and literature review identified six potential replacement primers which are chromate-free, have VOCs less than 340 g/l, and are commercially available. The six epoxy primer candidates identified are listed in Table VI.

TABLE VI - EPOXY PRIMER CANDIDATES

Manufacturer	Product Identification	Description
Deft	44-R-8A/44-W-7 (MIL-P-53030)	Water reducible
DeSoto	PR-330/ACT-330	High solids
Akzo	41407B534	Ultra-guard high solids
Lord Chemical	K3803A	Urethane, high solids
Savannah	D-213 Industrial Red	High solids
Gavlon	9815-8509	High solids

<u>Phase II.</u> During the initial screening tests, it was found that the Lord Chemical primer (K3803A) only had a pot life of 10 to 15 minutes. This candidate was eliminated. The screening test results for the remaining 5 candidates are presented in Table VII.

<u>Phase III.</u> The tests for GSE application were all included in the Phase II testing, thus no additional tests were needed for this application. The test results for the SRFH are presented in Table VIII.

TABLE VIII* - MIL-P-53030 PRIMER RESULTS FOR SRFH

TABLE VIII - IIILEY - 30000 THIME!! TIESGETG TO!! GIT!!				
Test	Coating	Result		
		Dett primer (MIL-P-53030)	9922 primer (control)	
Dry tape adhesion	primer	Pass	Pass	
Intercoat adhesion	primer & A276 white PU topcoat	Pass	Pass	
	primer & Z306 black PU topcoat	Pass	Pass	
Outgassing	primer	TML: 2.5 - 2.9% CVCM: 0.15 - 0.35%	TML: 2.0 - 2.1% CVCM: 0.04 - 0.05%	
	primer & A276 white PU topcoat	TML: 4.0 - 5.5% CVCM: 0.01 - 0.08%	TML: 3.8 - 4.8% CVCM: 0.02 - 0.03%	
	primer & Z306 black PU topcoat	TML: 1.4 - 4.9% CVCM: 0.04 - 0.14%	TML: 1.4 - 2.7% CVCM: 0.01 - 0.04%	
CTE, um/m°C	primer	$\alpha_1 = 29.2$	$\alpha_1 = 40.7$	
• Test 1		$\alpha_2 = 73.8$	$\alpha_2 = 52.6$	
CTE, um/m°C	primer	$\alpha_1 = 23.8$	$\alpha_1 = 48.6$	
• Test 2		$\alpha 2 = 675$	$\alpha_2 = 852$	

^{*} All outgassing and adhesion were accomplished in accordance with thickness and cure schedules called out in SRFH paint processes documents.

Wash Primers

Only one wash primer candidate (Deft, 46-W-4) was identified that was both chromate-free, had a VOC less than 420 g/l and was commercially available. It was tested against the current MIL-C-8514 wash primer for adhesion and compatibility. Results comparing the wet tape adhesion of Deft wash primer to the current MIL-C-8514 wash primer are presented in Table IX. Both wash primers had some failures depending on which substrate, primer and topcoat were used. There is no wet tape adhesion requirement in MIL-C-8514. Additional tests are presented in Table X.

TEST	DEFT	DE SOTO	SAVANNAH	GAVLON	AKZO
/iscosity-initial	26 seconds	25 seconds	Too thick	Too thick	15 seconds
Viscosity-spray	26 seconds	25 seconds	19 seconds	18 seconds	15 seconds
Outgassing: CVCM	0.073%	0.002%	0.07%	0.40%	0.26%
TML .	1.92%	3.86%	3.07%	2.73%	5.10%
Dry Time: Tack-free	30 minutes	2.5 hours	60 minutes	30 minutes	14 hours
Dryhard	1.0 hours	3.5 hours	2.5 hours	2.0 hours	22 hours
Appearance	Pass	Pass	Pass	Pass	Pass
ifting	Pass	Pass	Pass	Pass	Pass
Knife test	Pass	Fails	Pass Pass	Pass	Pass
mpact resistance	30%	4%	30%	20%	30%
Water resistance	Pass	Pass	Pass	Pass	Pass
Salt spray resistance	Pass	Fails	Fails	Pass	Pass
Filiform corrosion resistance	Pass	Fails	Pass	Pass	Pass
Fluid Resistance: Lube oil	Pass	Pass	Pass	Pass	Pass
Hydraulic oil	Fails	Pass	Pass	Pass	Pass
Gloss	3 units	15 units	0.9 units	1.5 units	29 units
Volatile organic content	280 g/l	339 g/l	471 g/l	401 g/l	287 g/l
Adhesion: (Wet Tape)					
2024 A1 with MIL-C-5541, Cl. 1A	Pass	Fails	Pass	Pass	Pass
2024 Alclad, solvent cleaned	Fails	Fails	Fails	Fails	Pass
2024 Alclad, with TT-L-32 topcoat	Pass	Fails	Pass	Fails	Pass
6061 Al, solvent cleaned	Fails	Fails	Fails	Fails	Pass
6061 AI with MIL-C-5541, Cl. 1A	Pass	Pass	Pass	Pass	Pass
Steel, solvent cleaned	Pass	Pass	Fails	Fails	Pass
Steel, sandblasted	Pass	Pass	Fails	Fail s	Pass
Adhesion: (Dry Tqpe)					
2024 Al with MIL-C-5541, Cl. 1A	Pass	Fails	Pass	Pass	Pass
2024 Alciad, solvent cleaned	Pass	Pass	Pass	Pass	Pass
2024 Alclad, with TT-L-32 topcoat	Pass	Pass	Pass	Pass	Pass
6061 Al, solvent cleaned	Pass	Fails	Pass	Pass	Pass
6061 Al with MIL-C-5541, Cl. 1A	Pass	Fails	Pass	Pass	Pass

TABLE IX - WASH PHIMER WET TAPE ADHESION TEST RESULTS

	Coating	Substrate		
Wash Primer Topcoat			Bare Steel	6061 Al
Deft 46-W-4	MIL-P-53030	MIL-R-85285	Pass	Pass
	MIL-P-23377	MIL-R-85285	Fails	Pass
	MIL-P-85582	MIL-R-85285	Pass	Fail
MIL-C-8514	MIL-P-53030	MIL-R-85285	Pass	Fail
	MIL-P-23377	MIL-R-85285	Fails	Pass
L	MIL-P-85582	MIL-R-85285	Pass	Fail

TABLE X - WASH PRIMER TEST RESULTS

Coating	Substrate	Test	Result
Deft 46-W-4	N/A	Dry time	Tack Free: 30 min. Dry hard: 1 hour
Deft 46-W-4	N/A	VOC	183 g/L
Deft 46-W-4	Steel	Appearance	Pass
Deft 46-W-4 MIL-P-53030 MIL-R-85285	Steel	Adhesion, FTMS 141, Method 6301 w/o cuts	Pass

DISCUSSION

Epoxy Primers

The primary function of epoxy primers is to (1) increase its compatibility between the substrate and the topcoat, (2) improve adhesion, and/or (3) improve the corrosion resistance of the substrate. The process screening tests include tests to verify that the primers will function as required, evaluate the application characteristics (i.e. dry time, appearance) of the coating, and verify BAAQMD VOC requirements are met. The process screening tests (see Table II) were derived from MIL spec requirements for paint primers (i.e. MIL-P-23377 - Primer Coatings: Epoxy, Chemical and Solvent Resistant).

A major concern in using chromate-free primers is the potential loss of corrosion resistance. Filiform corrosion resistance and salt spray resistance are two tests that evaluate corrosion resistance. In filiform corrosion resistance, primed and topcoated panels are "X" scribed, placed in concentrated hydrochloric acid for an hour, and then placed in a chamber at 104F and 85% relative humidity for 1000 hours. Filiform corrosion appears as threadlike filaments initiating from the exposed substrate and spreading underneath the coating. The test simulates damage to the surface of a piece of hardware and how well the primer prevents further coating damage. In salt spray resistance, primed panels are "X" scribed and placed in a 5% salt fog chamber. Salt spray is intended to reproduce corrosion that occurs in salt spray conditions. MIL-P-53030, Gavlon, and Akzo all passed both filiform and salt spray corrosion resistance. Savannah passed filiform but failed salt spray resistance. The DeSoto primer failed both of the corrosion resistance tests.

MIL-P-53030 had good wet tape adhesion on alodined aluminum and bare and sandblasted steel. Akzo passed all the wet tape adhesion tests. Both Savannah and Gavlon passed wet tape adhesion on alodined surfaces but struggled on bare surfaces and sandblasted steel. DeSoto failed most of the wet tape adhesions on both bare and alodined aluminum. All but DeSoto passed all the dry tape adhesion testing.

MIL-P-53030's ease of application and one hour dry time help make it practical for manufacturing to use. Akzo was also easy to apply but has a long tack-free time (14 hours) and dry hard time (22 hours) which can be inconvenient for manufacturing to use. The DeSoto primer was easy to handle but was brittle, contributing to the aforementioned failures in adhesion. Both Gavlon and Savannah handled adequately and had acceptable dry times but both required significant solvent thinning to reach spray viscosity. The Lord primer had a pot life of 10-15 minutes. Lord indicated that their K3803A primer was designed for a two-component spray gun. Two feed lines separately pump the two components together into a constantly agitated pot, and then feed the mix to the spray gun to be applied to the surface of the part. This application is not practical for LMSC so testing was halted.

The VOC was tested using BAAQMD Method 22 (Solvent based, less than 2% by weight water) or Method 23 (Water based). MIL-P-53030, DeSoto, and Akzo all were VOC compliant at application viscosity. Both the Gavlon and

Savannah primers were designed as high solids but their vendors did not test their VOC's according to the BAAQMD methods. For example, in Gavlon's case, they used theoretical solids instead of actual in calculating their VOC.

Ground Support Equipment. The MIL-P-53030 primer met all engineering requirements needed for a GSE paint primer. MIL-P-53030 was compatible with MIL-C-22750 epoxy topcoat, MIL-C-85285 high solids polyurethane, and epoxy enamel used on GSE at LMSC. That makes it an excellent choice to replace MIL-P-23377 high solids chromated paint primer and MIL-P-85582 water reducible chromated paint primer. Further testing of Akzo is warranted but not a high priority due to its long dry time and the success of finding MIL-P-53030. It is still being considered as a second chromate-free primer for GSE. No further study was deemed necessary on Savannah, DeSoto, or Gavlon primers.

Space Related Flight Hardware. In Phase II testing, the MIL-P-53030 primer results were encouraging, so it was evaluated for possible use on space related flight hardware (SRFH). MIL-P-53030 was compared to the current high VOC, chromated primer for SRFH, Chemglaze 9922.

Outgassing is one of the key requirements for a coating used in space environments. When a coating is exposed to space vacuum environments, some volatiles can condense on critical surfaces and interfere with performance of optical or thermal control surfaces. ASTM E 595 is the standard method for measuring outgassing in a vacuum environment. ASTM E 595 requirements for Total Mass Loss (TML) and Collectible Volatile Condensable Material (CVCM) are 1.0% max and 0.1% max, respectively. MIL-P-53030 by itself has CVCMs ranging from 0.15% to 0.35%. When MIL-P-53030 is topcoated with A276 gloss white polyurethane or Z306 flat black polyurethane the CVCM of the composite films is consistently under 0.1% and the TMLs compare favorably with the current Chemglaze 9922 system (see Table VIII).

Intercoat adhesion with the two different SRFH topcoats, A276 gloss white polyurethane and Z306 flat black polyurethane, is important and MIL-P-53030 has been found to be compatible with both.

Substrate adhesion to several different SRFH surfaces is also important. Only dry tape adhesion is necessary as water and other weather considerations are non-existent in space environments. MIL-P-53030 has demonstrated good adhesion to alodined 6061 aluminum, bare 6061 aluminum, Dow 17 coated magnesium, and abraded epoxy graphite.

The CTE of the two primers were compared in order to identify any gross differences in thermal characteristics between the two materials. The CTE for MIL-P-53030 primer compares favorably with that of the Chemglaze 9922 primer.

Further work includes outgassing rate studies and thermal cycling (-250F to +250F).

Wash Primers

After comparing the wet tape adhesion of the Deft wash primer and MIL-C-8514 wash primer with different primers on different substrates (see Table IX), it was noted that both the control (MIL-C-8514) and the Deft wash primer performed erratically and did not meet the requirement consistently. Neither MIL-C-8514 (Metal Pretreatment Coating Compound) nor DOD-P-15328 (Pretreatment Wash Primer - Formula No. 117 for Metals) specifications have any wet tape adhesion or weathering test requirements. It was decided that the wet tape adhesion requirement was not necessary.

It should be noted that all the wet tape adhesion failures for both MIL-C-8514 and Deft were between the wash primer and the substrate. The Deft wash primer demonstrated acceptable intercoat adhesion with three different primers. Two of the primers, MIL-P-85582 water reducible, epoxy primer and MIL-P-23377 high solids, epoxy primer, are chromated and have been replaced in the SSD GSE paint processes specification by the third primer, MIL-P-53030 epoxy primer.

The subsequent tests for the Deft wash primer (Table X) indicated that it is an acceptable chromate-free replacement. The Deft wash primer passed VOC, appearance, and adhesion tests. This adhesion test was a wet tape adhesion with no cuts. The Deft wash primer is easy to apply and convenient to use since a subsequent primer can be applied after an hour. Since it is VOC compliant and performs very well with the GSE MIL-P-53030 primer, it was implemented as the GSE wash primer for SSD.

CONCLUSION

Ground Support Equipment

Two epoxy primers, MIL-P-53030 and Akzo, were found that meet GSE requirements. MIL-P-53030 primer has the advantage of a short dry time which makes it convenient for manufacturing to use and it has been implemented. Akzo is still under consideration but due to its long dry time and the success of finding another successful candidate, there is not urgency to test further at this time.

Space Related Flight Hardware

MIL-P-53030 has shown much promise as an eventual replacement for use on SRFH. Further work includes outgassing rate studies, thermal cycling (-250F to +250F).

Wash Primers

The Deft wash primer met all the requirements of GSE wash primer. Since it is VOC compliant and performs very well with the GSE MIL-P-53030 primer, it was implemented as the GSE wash primer for SSD.

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

AN INVESTIGATION OF FLEXIBILITY TEST METHODS FOR LOW VOC AEROSPACE COATINGS

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INTRODUCTION

Throughout industry, development work is currently underway to find low volatile organic compound (VOC) containing alternatives to high performance aerospace coatings. Chemical resistance and flexibility are two performance characteristics required of aircraft coatings. Unfortunately, these two requirements trade off with each other - increasing one decreases the other. Impact and mandrel bend tests are defined for the flexibility requirements in current aerospace coating specifications. As low VOC alternatives are being formulated and evaluated, the suitability of these test methods to represent the actual functional requirements of an aircraft in service has been questioned. The relationship of the results of current flexibility test methods to each other and to actual functional performance will be studied using a test set-up representative of service conditions.

ENVIRONMENTAL SIGNIFICANCE

In the course of developing environmentally compliant coatings, chemists and engineers are forced to look to new binder technologies. Among the more promising new technologies at this time are water-borne, high solids, ultraviolet (UV) curable and powder coatings. Mechanical test methods are often used in aerospace specifications to assess coating performance. In this paper, a mechanical test is a test that measures the performance of a coating, as compared to a test that measures the physical properties of the material, such as the glass transition temperature. Adhesion, abrasion resistance, flexibility, and hardness are examples of requirements where mechanical tests are used. These test methods can be successfully used when measuring relative performance of similar coating formulations. When used to assess the properties of a new formulation, these mechanical test methods may not provide definitive results. If these mechanical tests are used without good judgement, viable candidate formulations may be discarded as unusable. During the course of developing environmentally compliant coatings, unnecessarily limiting the number of viable alternatives would be unfortunate. A study of flexibility test methods and their relationship to functional requirements in aerospace applications will provide data to support engineering judgement.

AEROSPACE REQUIREMENTS

Coatings used in the aerospace industry have a unique set of requirements. They must withstand a variety of environmental conditions during flight, ground handling, storage, and sortie and mission situations. They must also withstand extreme combinations of these environmental conditions, such as high temperature and chemical exposure. Table I summarizes the common environments and their potential detrimental effects ¹.

Environmental Condition	Effect
High Temperature	expansion of substrate
Low Temperature	contraction of substrate, embrittlement
Thermal Shock	physical stress
Humidity Extremes	moisture absorption, embrittlement
Low Pressure	outgassing
Vibration	physical stress
Liquids (fuel, water, hydraulic fluid, solvents, lubricants)	chemical attack, softening, swelling, blistering
Polluted Atmosphere	degradation
Ice, Hail, Snow	erosion, moisture absorption
Fungi	degradation
Ozone	chemical attack, degradation
Sand, Dust	erosion
Solar Radiation	physical degradation, embrittlement, discoloration

Table I - Environmental Conditions for Aerospace Coatings

The typical finish configuration on aluminum aircraft structure is an inorganic surface treatment, one coat of corrosion inhibiting epoxy primer, and two coats of a polyurethane topcoat.

Flexibility verses Chemical Resistance

In the course of the development of new, environmentally compliant coating materials for use in the aerospace industry, the issue of flexibility requirements combined with chemical resistance requirements is mentioned time and time again as a roadblock. Current coating technology relies on controlling the extent of cross-linking that exists in the coating to achieve the required flexibility and chemical resistance. However, increasing the cross-link density to enhance chemical resistance is detrimental to the flexibility of a coating, while decreasing the cross-link density to improve flexibility compromises the chemical resistance properties.

When the flexibility of a coating is considered independently as a mechanical property, the actual relevant requirement in aerospace applications is that the coating not crack in service around fastener heads, and at laps and at gaps in the structure. Flexibility is required to withstand the relative motion between two separate but continuously coated pieces, such as structure and fastener, due to vibrational and thermal stresses. One of the primary functions of aerospace coatings is corrosion protection, and a break in the coating reduces its ability to protect the substrate on which it is applied. Both requirements are vital to the successful high performance aerospace coating formulation.

Resistance to a variety of different chemicals is also a fundamental requirement of these coatings. These chemicals include fuel, hydraulic fluid and solvents. They may be encountered during the assembly of aerospace hardware as well as in service. In service, coated surfaces will be literally bathed in these substances. The chemical resistance of a coating can be tested directly by immersing coated panels, by taping a saturated cloth onto coated hardware, or by rubbing a saturated cloth back and forth across the coating surface.

CURRENT TEST METHODS

Material specifications for coatings used in the aerospace industry typically require one or more of four different types of tests to evaluate a coatings "flexibility". These four types of mechanical tests are forward impact resistance, reverse impact resistance, room temperature mandrel bend and low temperature mandrel bend. Other types, which are used occasionally and will not be discussed in this paper, include free-film elongation and tensile strength.

Impact Resistance Test

The impact resistance test measures the ability of an applied coating to resist the effects of an impact that occurs at a rapid rate. The forward impact resistance test places a coated panel into a fixture. A known weight is dropped from various heights onto a rounded indenter resting on the surface of the coated face of the test panel. A reading of the highest value of inch-pounds (in-lbs) at which the coating does not crack is obtained. The reverse impact test is similar, except the panel is placed coating side down.

Mandrel Bend Test

Bend tests measure the size of the radius around which a coated panel can be bent before cracking. The coated panel is placed into a fixture and is bent with a roller around either a cylindrical or a conical mandrel. When a cylindrical mandrel is specified, the test usually has a pass/fail criteria around a given mandrel radius. A conical mandrel has a radius that goes from approximately two inches to one-eighth inch. In the conical mandrel bend test, a percent elongation value is obtained by measuring the length of the crack from the small radius end. This test is also performed at low temperature, typically at -65 °F.

Problems

These typical test types are used both interchangeably and as measures of the separate properties of flexibility and impact resistance. How the requirements are defined varies from one specification to the next. For example, the forward and reverse impact resistance test appears in various coating specifications under the name impact resistance, impact durability, impact flexibility, and ambient flexibility, to name a few. This generates confusion as to what property is actually being measured. The mandrel bend test does not evaluate the coating performance in a situation similar to service; aerospace coatings in service do not undergo bending around tight radii.

Mechanical tests that are used in specifications are typically quick, inexpensive and simple to run. Often these tests are either pass/fail or have qualitative rather than quantitative results. These mechanical tests are valuable as receiving and inspection, and quality control tools. These types of tests can be successfully used when comparing a set of similar materials. However, when the test is expanded to compare two different types of materials, direct comparisons can no longer be made.

Qualified coatings must maintain their properties while being subjected to extremes of temperature and humidity, as well as chemical attack and solar radiation. Typically, the mechanical tests are performed on freshly applied coatings. When qualifying new materials, however, some specimens for the various flexibility tests are exposed to either accelerated or natural weathering prior to testing. Allowing the test specimens to undergo weathering prior to testing is one way to increase the severity and realism of these tests. However, it does not duplicate service conditions. The problems with relying on these simple mechanical tests are compounded by the fact that the material that is being worked with is viscoelastic in nature. That is, the coating's behavior changes with temperature as well as with the rate of applied stress. All of these factors contribute to the complexity of understanding how to properly use mechanical test data.

If new coating formulations perform marginally when subjected to these tests and are compared to established coating technologies, they may be discarded as unusable. If these formulations have greater stability of physical properties under service conditions, or have better adhesion, they may in fact be viable for use in aerospace applications. Obtaining data will support scientific judgement in these areas.

TEST PLAN

Objectives

The dilemma of chemical resistance verses flexibility and the question of proper application of current test methods has been highlighted during the course of developing new coating technology in the search for low VOC coatings. This has caused many coatings vendors to question the requirements and the use of current flexibility test methods. While many of the problems associated with the use of these test methods are intuitively apparent, no actual data was found to address the vendors concerns. To begin to address the questions of the proper application of existing flexibility test methods, a study of these methods was planned. In order to keep the scope of the study manageable, it was decided that only a small set of variables would be incorporated. The affects of conditions such as thermal shock or erosion will not be considered.

The following is a list of objectives around which this test was planned:

1) Obtain data comparing each of the four typical test methods to each other, using rank correlation as the evaluation criteria.

- 2) Develop and perform a test method that represents aerospace service conditions, and compare the results to current test method results.
- 3) Use a designed experiment in order to minimize expense of test and to obtain data on impact of components of coating system on test results.
- 4) Determine if further, detailed study of this issue is warranted.

Development of Representative Service Life Test. Coatings on aircraft are applied in a continuous layer over an assembly of parts. These coatings must have the flexibility to withstand the relative motion of these parts due to vibrational and thermal stresses. A test that would simulate this type of service environment would require a stress be applied to a specimen configured such that there would be relative motion between two parts. It was determine that a tension-tension fatigue test performed on a fastened lap joint would provide this test scenario. Table II summarizes the test set-up. The tension-tension fatigue test is a common test in the aerospace industry for evaluating the mechanical properties of materials. For the purposes of this study, it provides the relative motion and repetitive stress environment that is representative of the service conditions faced by aerospace coatings. The test specimen, which is described in Figure 1, is made of 2024-T3 aluminum sheet fastened with fifteen countersunk-head hex-drive fasteners. The aluminum sheet was surface treated in accordance with Mil-C-5541 - "Chemical Conversion Coatings for Aluminum Alloys" - or Mil-C-8625 - "Anodic Coatings for Aluminum and Aluminum Alloys". The specimens were assembled with fay surface sealant and the fasteners were wet-installed with the same sealant. One coat of primer and two coats of topcoat were applied after assembly.

Test type	tension-tension fatigue
Max load	15,000 and 18,500 lb
Max stress	13 and 15.9 ksi
Min stress/Max stress Ratio	.019
Temp./Humidity	ambient

Table II - Summary of Test Set-up

In this structural fatigue test, each end of the specimen is clamped into the fixture and a load is applied that places the specimen into tension. As the cycles of the test progress, the samples is repeatedly placed into more and less tension. The load is never completely removed. Because the sample is not symmetrical, the outside three rows of fasteners are placed into greater tension than the center row.

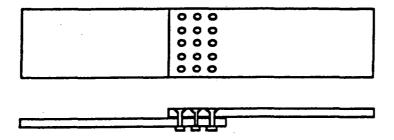


Figure 1 - Representative Service Life Test Specimen Configuration

Detailed Test Plan

The variables chosen for this designed experiment were (1) surface treatment, (2) primer flexibility, (3) topcoat flexibility, and (4) weathering. Varying these four factors provides information on the variety of different test configurations that may appear in aerospace coating specifications. The addition of replicate specimens without primer completes the coverage of potential specification configurations. While the test was designed around these four variables and their interactions, the data presented in this paper examines only the first three. An analysis of a three-factor subset of this test design will not yield information concerning interactions between the factors. The complete analysis, incorporating data with all four of the variables, will provide information on all of the possible interactions.

Design of experiments was used to develop the test matrix. The matrix describing the panel configurations comprising a set is shown in Table III.

Run	Surface Treatment	Primer Flexibility	Topcoat Flexibility	Weathered
1	Mil-C-5541	high	low	no
2	Mil-C-5541	high	high	yes
3	Mil-C-5541	low	low	yes
4	Mil-C-5541	low	high	no
5	Mil-C-8625	high	low	yes
6	Mil-C-8625	high	high	no
7	Mil-C-8625	low	low	no
8	Mil-C-8625	low	high	yes

Table III. Flexibility Requirement Test Matrix

The test begins with an evaluation of the test methods themselves and yields data on how well the test results for each test method correlate with each other. Seven sets of runs were performed using 4 x 6 x 0.020 inch aluminum panels, with four replicates of each. These seven sets include configurations with and without primer. The four flexibility test methods chosen for this study are forward impact, reverse impact, room temperature conical mandrel bend and low temperature conical mandrel bend.

The coatings selected for this study of flexibility test methods are shown in Table IV. Both of the high flexibility choices claim to have sixty percent elongation when tested with a G.E. impact tester and both of the low flexibility coatings claim twenty percent elongation.

Coating	High Flexibility	Low Flexibility
Primer	Koroflex	MIL-P-23377 Class 1
Topcoat	Gloss MIL-C-83286	Flat MIL-C-83286

Table IV. Coatings Selected for Flexibility Test Study

A tension-tension fatigue test of a fastened lap joint was chosen to represent service conditions. The finish configurations defined in the test matrix (see Table III) were applied to this lap-splice fatigue specimen. The mechanical test resulted in data on the number of cycles to onset of cracking. The data generated in this study will be analyzed statistically, looking at the finish configuration as a system as well as at the individual finish components.

DATA AND RESULTS

Analysis Methods

Based on the use of a designed experiment, the individual contribution of each of the three factors - surface treatment, primer flexibility and topcoat flexibility - on the performance of the tested panels can be determined statistically. The results of this analysis can be seen graphically in figures 2 through 6. Table V provides information about the codes used on the x-axis of these charts.

Code Letter	Finish Used
A	Mil-C-5541
В	Mil-C-8625
C	Low Flexibility Primer
D	High Flexibility Primer
E	Low Flexibility Topcoat
F	High Flexibility Topcoat

Table V - Explanation of Codes Used in Figures 2 Through 7.

Impact Resistance Test Results

Figures 2 through 5 show the results of a statistical analysis of the results of impact testing. This analysis shows the contribution of each of the three factors to the results obtained during the test. It does not account for interactions. The analysis of the topcoat used is confounded with the interaction between the surface treatment and the primer. Once the entire test matrix, as shown in Table III, is complete and analyzed, the information about the contribution of all interactions will be obtained.

The forward impact test results shown in Figure 2 show that either the topcoat or the surface treatment/primer interaction has the most significant contribution to the test results. Because the effects of the surface treatment and the primer do not appear to be significant, it may be assumed that this contribution is in fact attributed to the topcoat. The reverse impact test results shown in Figure 3 show a significant contribution to the test results by both the primer and the topcoat. Therefore, the possibility of a strong surface treatment/primer interaction cannot be discounted.

Test panel configurations without primer were also tested. Figure 4 shows the results of the forward impact test. Neither the topcoat nor the surface treatment had a significant contribution to the test results. The results of the reverse impact resistance test on panels without primer is shown in Figure 5. These results clearly show that the topcoat properties had the more significant contribution to the test outcome.

Forward Impact Resistance

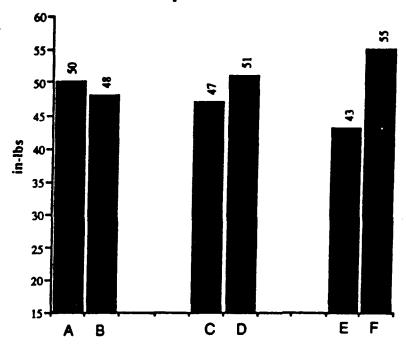


Figure 2 - Forward Impact Resistance Tests Results - Factor Effects (see Table V)

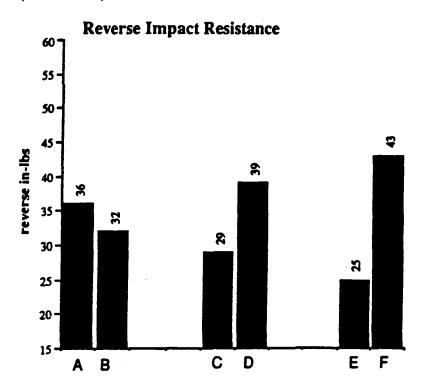


Figure 3 - Reverse Impact Resistance Test Results - Factor Effects (see Table V)

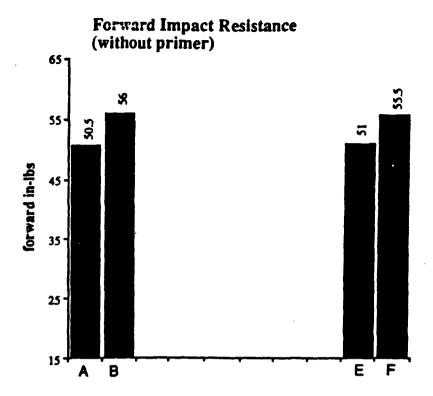


Figure 4 - Forward Impact Resistance Test Results - Factor Effects WITHOUT Primer (see Table V)

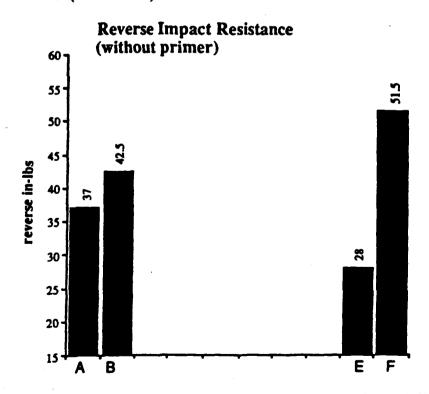


Figure 5 - Reverse Impact Resistance Test Results - Factor Effects WITHOUT Primer (see Table V)

Conical Mandrel Bend Test Results

All of the panels tested in the room temperature conical mandrel bend tests passed without any cracking. Those tested at the low temperature of -65 °F did have some failures, to which a percent elongation value could be assigned. No quantitative values could be assigned to those that passed. Because of this, the same type of analysis that was done on the impact resistance tests and the service life test could not be done on the mandrel bend data. Additionally, the two configurations that experienced failures both had inorganic surface treatments in accordance with Mil-C-5541 and were primed with the low flexibility primer. In all of the failures, the cracks were accompanied by significant loss of adhesion of the surrounding coating. The disbond, in every case, occurred between the conversion coating and the substrate. This may be due to inadequacies in the applied surface treatment.

Representative Service Life Test Results

Two replicates of each of the four configurations were fabricated for fatigue testing in this study. A steep learning curve was experienced during the testing of the first set of replicates. which was performed at a maximum load of 18,500 pounds. Because this type of test had not been performed before, no experience was available concerning when to expect the first cracks. An estimate was made that the first cracks would appear around one thousand cycles. This was a poor estimate. Actual first cracks appeared before five hundred cycles. Consequently, inspections for cracks were not made at the necessary cycle intervals to obtain differentiation in the data on the first four specimens. Additionally, it was determined that decreasing the load on the parts would create greater spread in the data. The second set of replicates was run at a lower load of 15,000 pounds and inspections for cracks were taken every ten cycles during the beginning of the test. Data points were taken at the number of cycles when cracks around three fastener heads were observed. This data is shown in Table VI and Figure 6. This data is based on only one replicate. so little confidence may be placed on the statistical analysis. Additionally, one of the configurations performed much better than the other three, so that single data point distorts that data shown in Figure 6. The data did, however, illustrate a significant difference between the performance of each of the four different test configurations.

Run Configuration (see Table III)	Cycles to Onset of Cracking
1	50
4	10
6	500
7	30

Table VI - Raw Data for Representative Service Life Test

In all cases the cracks began around the tops of the fastener edges in the top row of fasteners. Once the cracks were initiated at the top of each of the fifteen fastener heads, crack size did not change significantly over the next several thousand cycles. In some cases, bubbles in the coating appeared and grew at the edge of the fastener heads. These bubbles were due to loss of adhesion without a break in the film. In other cases, the fastener rotated significantly in the hole while cycling, causing a twisting and stretching effect around the edges of the fastener heads. In these cases, the coating eventually tore with jagged edges. While testing the specimen with the configuration of low flexibility topcoat over high flexibility primer, it was observed that only the topcoat cracked. After ten thousand cycles, all but a few of these cracks continued to show primer, intact, under the topcoat crack. All of the other test configurations cracked through the topcoat and primer from the outset.

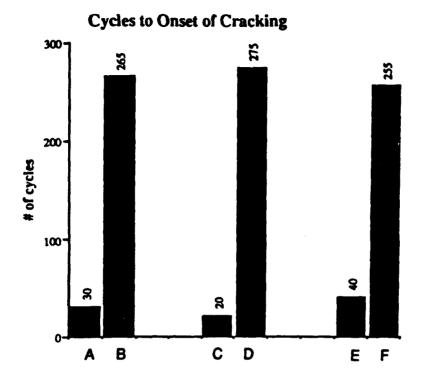


Figure 6 - Representative Service Life Test Results - Factor Effects (see Table V)

Comparison of Test Methods

Due to the small number of test configurations, an absolute correlation analysis was not performed at this time. This type of correlation will be performed after data is obtained for the entire test matrix (see Table III). Instead, the data has been analyzed by ranking the results of each test and comparing these rankings. This ranked data is shown in Table VII.

	RANK					
Run #	Forward Impact	Reverse Impact	Forward Impact	Reverse Impact	Low Temp Bend	Service Life Test
	With	Primer	Primer Without Primer			
1	3	3	2	4	3	2
4	2	2	4	2	4	4
6	1	1	1	1	1	1
7	4	4	2	4	1	3

Table VII - Ranked Data Comparison Between Test Types

The averaged raw data is shown in Table VIII. Each entry in this table is the arithmetic mean of four replicates.

	AVERAGED RAW DATA					
Run #	Forward Impact	Reverse Impact	Forward Impact	Reverse Impact	Low Temp Bend	Service Life Test
	With Primer		Without Primer			
1	46 in-lb	32 in-lb	51 in-lb	28 in-lb	5% elong	50 cycles
4	54 in-lb	40 in-lb	50 in-lb	46 in-lb	>17%	10 cycles
6	56 in-lb	46 in-lb	61 in-lb	57 in-lb	>17%	500 cycles
7	40 in-lb	17 in-lb	51 in-lb	28 in-lb	4% elong	30 cycles

Table VIII - Averaged Raw Data for All Tests

FUTURE WORK

The effort to complete the gathering of data in accordance with the test matrix shown in Table III is ongoing. Replicates of all of the test configurations for this test plan are currently undergoing accelerated weathering. The one exception is the lap-splice fatigue specimens. These specimens are large and bulky and will be difficult to handle in existing accelerated weathering equipment. Due to lack of available funds, no additional replicates of the tension-tension fatigue test configurations already tested will be evaluated. Once the entire data set is gathered, a more rigorous statistical analysis, examining main factor effects as well as interactions, will be performed. The results of this analysis will provide a more substantial comparison of the results of the different test methods and will indicate whether additional testing, incorporating more complexity of variables, is warranted.

DISCUSSION AND RECOMMENDATIONS

Impact Resistance Test

An examination of the averaged raw data in Table VIII shows a greater data spread in the reverse impact resistance test than in the forward impact resistance test. It also demonstrates that the reverse impact test is a more severe test than the forward impact resistance test. This indicates that the reverse impact resistance test is the better choice when comparing different finish configurations. This is particularly true when comparing adjustments of the same basic coating formulation. The possible existence of a strong surface treatment/primer interaction suggests that adhesion plays a role in the performance of a coating configuration in the reverse impact resistance test.

The topcoat flexibility had the most significant impact on the test results obtained in the forward impact resistance test on the configurations used in this study.

Conical Mandrel Bend Test

The type of failure observed on those configurations that cracked during the low temperature mandrel bend test suggests adhesion problems resulting from poorly treated substrates. Each of these panels were treated with a chemical conversion coating. However, all of the panels that received this treatment did not fail. Those that failed were the ones that were coated with the low flexibility primer. This suggests both a surface treatment/primer interaction and process problems with the chemical conversion coating. Additional replicates of this test will be run on freshly treated panels in order to further evaluate this finding and ensure that adequately processed panels have been used. Completion of data gathering for the entire test matrix will also provide information on the significance of a surface treatment/primer interaction.

The fact that there were so few failures in this test suggests that the conical mandrel bend test can be successfully used as an indicator of gross problems, but will not provide sound data on which to base fine comparisons. The low temperature mandrel bend test will be useful when screening prototype coatings. Performing the mandrel bend test at room temperature does not appear to be a useful test on the type of coatings that are typical in the aerospace industry.

Representative Service Life Test

Data on the number of tension-tension fatigue cycles to the onset of cracking of the coating around the fastener heads of a lap-splice specimen can be successfully obtained. The results, shown in Table VIII, show differentiation in the test results from one test configuration to another. It is recommended that future tests of this type be run at lower loads in order to further spread that data. The tests should be stopped and inspections made every ten cycles during the beginning of the test until greater experience is obtained to predict failure points. Multiple replicates, if they do not indicate significant variability, will also provide greater statistical confidence in the test results. A reliability-based analysis, examining the fraction failed as a function of the number of cycles, may also provide useful information.²

Comparison of Test Methods

The six tests that illustrated a difference between the performance of each of the different test configurations consistently ranked the same high flexibility primer/high flexibility topcoat configuration as the highest performer. Unexpectedly, the low temperature mandrel bend test revealed the low flexibility primer/low flexibility topcoat configuration as a high performer as well. All of the other five tests ranked this configuration low, with the exception of the forward impact test without primer, which is discussed below. It appears that adhesion may play a significant role in the performance of panels during this type of test. Completion of the entire test matrix and the performance of confirmation runs may shed more light on this phenomenon.

It appears that the forward impact resistance test performed on panels without primer yields data whose ranking is inconsistent with the test on panels with primer. A closer examination of the averaged raw data shows that three of the configurations actually yielded essentially the same results. Therefore, there is no inconsistency.

A meaningful comparison of ranked results shown in Table VIII for each of the three mechanical tests to the results obtained in the representative service life test cannot be made because the fatigue test data includes no replication. It appears, however, that the test does provide data that will differentiate between the performance of different coating configurations. Performing repeats of the test runs will provide a data set that could be statistically analyzed, resulting in more definitive results.

SUMMARY

Properly utilized, the mechanical test methods discussed in this paper can be valuable when comparing the performance of similar coating formulations. In the course of developing new coating technologies for environmental compliance, these tests will be relied upon as well. Evaluation of mechanical test results, when comparing different coatings, should not be done literally but should incorporate sound scientific judgement. The data presented in this paper and that will be obtained during this study will provide additional basis for informed coating selections.

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WATERBORNE MASKANT

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INTRODUCTION

Temporary protective coatings or maskants are heavily utilized in aerospace chemical processing operations. The purpose of a maskant is to provide protection to aerospace parts and assemblies during chemical and mechanical fabrication operations. Operations such as chemical milling, anodizing, painting, routing and bonding all require use of maskants to protect either the whole part or selected portions of the part from the chemical attack or mechanical damage.

These maskants can be of a solid form like tapes or rubber plugs, but they are more generally applied as liquids (like paints) which, when dry, conform to the contour of the part and are manually peelable after the processing is completed.

Traditional maskants have been rubber-based and require the use of chlorinated or aromatic solvents as the liquid diluent. Although successful in performance, these traditional solventborne maskants are highly toxic and have been the major source of air pollution from aerospace chemical processing factories. To combat this problem various approaches have been taken to either put pollution control devices onto the liquid maskant application equipment or to replace the solventborne maskants with less toxic and minimally polluting waterborne alternatives.

This paper discusses the chemical nature and challenges of successfully developed waterborne maskants. Current products produced by Malek, Incorporated which are on the approved specification lists of major aerospace companies are described. Details of the environmental benefits and manufacturing process advantages which result from the implementation of waterborne maskants are given. The economic considerations and pollution savings are described for two major aerospace processing factories located in the San Diego area.

ENVIRONMENTAL CONCERNS

Solventborne maskants are formulated in such a way as to dissolve water insoluble polymers. Solvents such as perchloroethylene, toluene and 1,1,1 trichloroethane are the most commonly used for this purpose. Although these solvents do dissolve the polymers, they must be used in a weight ratio of solvent to polymer of much greater than 1 to get proper flow characteristics. Therefore, solventborne maskants contain from 50 to 80 percent solvent which evaporates upon drying. All of these solvents are toxic to humans and the ecosystem in terms of

toxic air contamination, ground/soil poisoning, inhalation and transdermal absorption.

There are several local and federal regulatory agencies which control the of use and emission limits from maskant operations. Local air pollution control districts have rules which specifically call out the allowable solvent content and/or emission control efficiencies for aerospace maskant operations. The Environmental Protection Agency has also classified all of the above mentioned solvents as Hazardous Air Pollutants (HAPs). The Occupational Safety and Health Agency has set ever decreasing exposure limits for workers using these products. Public awareness of this has increased community concerns over companies involved with solventborne maskants. Companies may be required to do assessments of the health effects to the surrounding community resulting from their use of solventborne maskants. Finally, federal excise taxes are also being charged to consumers of these toxic solvents.

With all of this pressure being brought to bear on the usage of solventborne maskants, the industry is actively seeking alternative products.

SOLVENTBORNE AND WATERBORNE CHEMISTRY

The preferred alternative to minimize the many difficulties associated with the use of solventborne maskants has been to find low toxic air contaminant alternatives. In order to retain the good performance characteristics of the solventborne maskants, waterborne latices have been developed which are lower molecular weight, water dispersible counterparts of solvent-dilutable polymers. However, the emergence of these latices being commercially available only partially solves the problem, leaving many challenges to formulate a useful maskant.

Chemically, solventborne maskants are simple to understand and forgiving in nature. Large molecular weight polymers are used which generally are soluble in a variety of solvents. These large molecular weight polymers have sufficient chemical resistance "as is" so no chemical curing is required when the film dries. This contrasts with waterborne latex polymers which are of a smaller molecular weight and need to be cured or crosslinked with heat and/or additional chemical additives to achieve the desired chemical resistance and strength.

The other challenges have to do with the inherent differences between solvents and water. Solvents have generally low surface tension compared with water, therefore more care in handling must be taken to avoid bubbles or foam in the waterborne

maskant formulation. If the waterborne maskant formulation is frozen, it cannot be reconstituted by thawing out as can be done with solventborne maskants. This is due to the fact that latices are emulsions and the emulsion will generally not survive the shock of freezing. Water also supports bacterial growth and corrosion reactions on metal, so additives must be introduced to eliminate or control these phenomena.

Successful waterborne maskant formulators must consider these effects and have them addressed in their products.

MALEK'S WATERBORNE MASKANT LINE

Since 1988, Malek, Incorporated has successfully formulated waterborne maskants for aerospace chemical processing industries. An overview of Malek's current products are listed below.

PRODUCT	EMISSIONS* CONTENT	MAIN INDUSTRIAL USE	AEROSPACE COMPANIES
CAX-100-LA	70	Electroplating, Chemical Milling	Boeing, Pratt & Whitney McDonnell Douglas, Kelly AFB, Caspian Inc.
CAX-177	70	Chemical Milling	Boeing, Caspian Inc.
CAX-200+	70	Chemical Milling, Anodizing	Alenia, Italy, McClellan AFB, Caspian Inc.
MBP-100	20	Plating, Anodizing	General Dynamics Convair (McDonnell Douglas), Prat & Whitney, Kelly AFB

*In grams solvent per liter of coating

Malek's waterborne maskants have been used on production hardware since 1988 by Caspian Inc. in San Diego where they were pioneered for applications in chemical milling. Inherently low in solvent content and high in solids content these products all offer dramatic reductions in air emissions created when compared with their solventborne counterparts. As an example, the typical solventborne product contains 1200 grams of solvent per liter of coating at 20% by weight solids. The CAX products contain 70 grams of solvent per liter at 48% by weight solids. This results in a 95% reduction in solvent emissions per unit area masked. Malek's products are also applied in the same manner as with solventborne maskants, using conventional spraying, dipping and pre-mask cleaning techniques.

As you can see, Caspian Inc.'s early success inspired many other aerospace chemical processing companies to implement this technology. Although this industry is traditionally very conservative relative to changing processing chemicals, these products have proven themselves to be capable of meeting the strict requirements.

IMPLEMENTATION CASE STUDY: CASPIAN INC.

Caspian Inc. has operated an aluminum, titanium and steel chemical milling plant for over 25 years in San Diego, California. As a major subcontractor for the aerospace industry, Caspian Inc.'s chemical milling processes are approved by over twenty companies world wide, including Boeing, British Aerospace, Fokker (Holland), Grumman, Lockheed, Martin Marietta, McDonnell Douglas, Northrop, Rockwell, SAAB (Sweden), Short Brothers (Ireland), and Teledyne Ryan, to name a few.

Caspian Inc. recognized early on that the perchloroethylenebased maskant they were using would have to be replaced or be retro-fitted with a very expensive solvent capture system to recover greater than 90% of the emissions.

An economic analysis showed that the solvent capture system would cost greater than two million dollars to install and carry with it high operating and maintenance costs. Caspian Inc. also realized that even with this system, they would still be exposing the workers to perchloroethylene and the community would still have the risk of fugitive emissions as well as a potential gross emission if the recovery equipment were to fail, even momentarily. By working closely with Malek, Caspian Inc. examined its chemical milling process and current maskant application requirements and they successfully replaced their maskant operations with CAX-100-LA. They maintained all of their customer approvals and process profitability while reducing their emissions from maskant operations by over 95%.

The transition from a solventborne maskant process to the CAX process was remarkably straight forward. The main adjustment made by Caspian Inc. was to modify their maskant drying and curing process. Since solvents are much more volatile than water, it was not previously necessary for Caspian Inc. to use ovens or forced drying equipment. The new waterborne process requires that some provisions be made for drying the water. These provisions involved the purchase of portable heaters, a refurbishment of their existing oven and a minor adjustment to the normal process scheduling to allow this drying to occur. Although these changes cost Caspian Inc. capital and operating dollars (approximately \$30,000 for the heating equipment and 8 KWH of power) they were nearly insignificant when compared with

over \$2,000,000 in capital and at least 210 KWH operating cost for the solvent capture system.

Additionally, Caspian Inc. has achieved pollution banking credits of over 106 tons of VOC per year, which were awarded to Caspian Inc. as they decreased their air emissions well in excess of their currently permitted amount. These credits are a tangible financial asset for Caspian Inc. and they are valid as long as Caspian Inc. remains in business. Caspian Inc.'s community image is improved and they are receiving a wealth of positive publicity from environmental groups as well as customers who prefer that their work be done in the most environmentally conscious manner.

CASE STUDY: GENERAL DYNAMICS CONVAIR

General Dynamics Convair (GDC) has been in San Diego for over twenty years performing a wide variety of chemical processing, design and assembly of aerospace vehicles. In particular, GDC is a source of a section of fuselage of the McDonnell Douglas MD-11 aircraft. In the processing of this fuselage, a large quantity of the parts go through a chemical anodization process to promote paint adhesion to the interior's surface. The exterior of these polished aluminum skins are protected with maskant to prevent anodization of the exterior. San Diego Air Pollution Control District Rule 67.9 requires that by July 1, 1993, the maskant in this operation must have a VOC content of 250 grams per liter (less water and exempt compounds) or that an emissions control device must be installed to capture at least 90% of the solvent.

Similar to Caspian Inc.'s situation, GDC had an existing facility which would have been very expensive and technically difficult to retro-fit with solvent capture equipment. Their current spray booth was manually operated with airflow, humidity and temperature control. They did not normally oven cure their solventborne maskant, but they normally did allow the parts to completely dry in the spray booth (taking about one hour after all the spray coats are applied). Beginning in early 1992, GDC research personnel began testing of Malek's products for this The key specification factors involved the ability to resist all process solutions, no damage to the appearance of the highly polished aluminum, and easy manual peeling of the coating after anodization. GDC identified MBP-100 as the best waterborne alternative. Over thirty test pieces were run in GDC's production tanks to choose the coating and to determine the parameters, such as; required thickness, fluid viscosity, drying and curing times for optimum operations. By the middle of 1992, GDC had decided to go with a waterborne product in their current facility. Their facility engineers designed a simple oven to dry and cure the parts. This oven was placed onto existing floor space. No

modifications to the spray booth or spraying equipment were required. In late January 1993, the oven was installed and the first production parts were successfully produced at GDC using MBP-100.

Since then, GDC has stopped all purchases of solventborne maskant (1200 g/l emissions) and is using MBP-100 in its place, almost six months ahead of the required compliance date.

MBP-100, having only 20 g/l solvent content, saves over 98% on the emissions in every day use. Their spraying equipment can be cleaned with water and they do not need to add pure perchloroethylene to keep their maskant thinned.

The early reports from GDC are all positive. They have the performance they require, a competitive flow time, hugh pollution reductions and the workers are not exposed to highly toxic perchloroethylene.

CONCLUSION

Waterborne maskants for aerospace chemical processing do currently exist. These products cover the complete gambit of maskant utilization requirements. The fact that alternative technology does indeed exist is further verified by the fact that the local air pollution control district has recommended Malek's CAX waterborne maskant as best available control technology.

The option of conducting a solventborne maskant operation under the umbrella of a tightly-controlled solvent capture system has many disadvantages. These machines are very expensive to purchase and operate. They can contaminate the water which is used in the recovery process and their very intense energy requirements create increased pollution at the power plant.

Process flexibility is also compromised with a solvent recovery system in that the parts, when wet with solvent, must remain inside the device (a large, tightly-controlled building full of concentrated toxic vapors) until the solvent has completely evaporated. This requirement severely constrains part-flow time. All maskant operations must be halted if this device has any mechanical problems.

Waterborne maskants alleviate all of these problems while introducing very few negative features, such as drying time, which can be easily overcome with conventional technology. In general, aerospace processing companies using maskants have a

large degree of flexibility as to what products are used inhouse. Maskants do not fly-away with the airplane, and most times the individual companies themselves specify which products are used.

As can be seen by our wide ranging customers and processing applications list, many key companies which have been faced with the increasing environmental and health concerns have already implemented these and other waterborne maskant products. This number of companies is increasing dramatically, and waterborne maskants are now available from vendors of solventborne products. We at Malek, Incorporated truly feel that this can be a case where the industry acts with commitment and innovation to economically operate in a less polluting fashion.

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Low VOC Organic Coatings for Commercial Aircraft Application

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ABSTRACT

In response to the implementation of the 1970 Clean Air Act smog reduction requirements by state and local environmental regulatory agencies, over 300 low VOC (Volatile Organic Compound) paint formulations have been evaluated since 1985 by Boeing for use on commercial aircraft. These formulations have been state-of-the-art low VOC coatings based on (1) exempt solvent (methyl chloroform), (2) high solids, (3) water reducible, (4) powder, and (5) electrodeposition technologies.

Working closely with aerospace coatings suppliers, Boeing has achieved significant progress in the development and qualification of low VOC organic finishes, including corrosion resistant primers and decorative enamels used on the interior as well as on exterior components of our aircraft. Incorporating these new paints into our manufacturing processes, and those of our subcontractors is helping to reduce smog-forming emissions from aerospace facilities. Development efforts are continuing on low VOC coatings that can be used to replace the current (1) decorative paint system for interior plastic surfaces, (2) fuel tank primer, (3) flexible corrosion inhibiting coatings for in-spar areas of the wings, and (4) low VOC chromate-free primers for non-metallic composites and metallic surfaces.

BACKGROUND

The Clean Air Act of 1970 and implementation of its requirements by local environmental agencies such as the South Coast Air Quality Management District (SCAQMD) in the Los Angeles basin has posed a major challenge to both paint manufacturers and users. The major impact on coating of commercial airplanes was not felt until SCAQMD Rule 1124 mandated use of 350 g/l max. VOC primers by January 1, 1988 and 420 g/l max. VOC topcoats by July 1, 1990 for aerospace manufacturers in its jurisdiction¹. This had a very significant affect on Boeing commercial airplane manufacturing operations since hundreds of Boeing subcontractors are located in the Los Angeles area.

Similar requirements were also soon adopted by other environmental agencies such as those located in San Diego, San Francisco, Houston, Philadelphia, Wichita and Seattle. For the Seattle area, Puget Sound Air Pollution Control Agency (PSAPCA) Regulation II is requiring use of low VOC primers and topcoats for coating the interior fuselage areas of airplanes by January 1, 1994.

Significant investment in alternative materials development began in the mid 1980's, motivated by the company's desire to reduce use of VOC's in materials rather than relying solely on the use of control and capture technology. Use of control and capture technology requires very high capital investment as well as significant recurring maintenance costs including the cost of disposal of collected hazardous materials. Working with coating suppliers to develop, wherever possible, low VOC coatings that would perform equal to or better than the conventional primers and topcoats for commercial airplane application was considered to be the most environmentally sound and cost effective approach.

STATE-OF-THE-ART LOW VOC TECHNOLOGY

Several low VOC coating technologies were potential approaches to achieve lower VOC coatings. The following is a list of the these technologies including their advantages and disadvantages.

o 1,1,1-TCA Exempt Solvent

1,1,1-Trichloroethane (1,1,1-TCA, also called methyl chloroform) is considered to be non-photochemically reactive and exempt from VOC consideration by most regulatory districts. Since it is an organic solvent, 1,1,1-TCA is easier than water to use as a diluent in formulating coatings. These coatings have drying and application characteristics similar to conventional coatings. However, 1,1,1-TCA has been identified as an upper atmospheric ozone depleter and will be phased out of production by 1996.

o High Solids

Use of lower molecular weight resin is often necessary in order to maintain proper application viscosity with large reduction of VOC's in the coating formulation. Longer dry times, shorter pot lives and thicker films per coat are usually observed with high solids formulations.

o Water Reducible

One successful approach has been based on a modified polyamine and epoxy resin system which has been made water reducible with the addition of a nitroparaffin as solvent². This type of dispersion has demonstrated drying and application characteristics similar to conventional paint. However, it does require careful and gradual water reduction after the base and catalyst are mixed to secure a stable dispersion with proper viscosity. It has shorter pot life and shelf lives than the comparable conventional coatings.

o Waterborne

These coatings are water based dispersions that include water in either the base or catalyst or both and would usually require no further water additions. This is a relatively new development and has the potential advantages of increased pot life and easier mixing compared to water reducible coatings. Whether they can meet commercial aircraft performance requirements has yet to be verified.

o Powder

These are nearly 100% solids coatings emitting little or no VOC. The current state-of-the-art powder technology typically requires a minimum 250 F bake. Exposing some aluminum alloys to 250 F may have an adverse effect on their mechanical properties. In addition, this technology is applicable only to detail parts and is more difficult to get smooth aesthetically acceptable coatings.

o Electrocoating

This primer technology can offer very low VOC emissions, uniform film thickness and can incorporate the coating operation into a tankline surface preparation process. However, like powder, these materials typically require a minimum 250 F bake and are limited to detail parts applications. To date, corrosion performance has been lower than the current conventional primers possibly due to lower levels of chromates.

COMMERCIAL AIRPLANE LOW VOC PAINT DEVELOPMENT

Boeing has worked with aerospace coating suppliers to identify potential state-of-the-art low VOC coating technologies that can be used to replace the conventional high VOC coatings. The most critical criterion is that they provide at least equivalent service performance. Since 1985, over 300 primer and topcoat formulations have been evaluated (Table I). As a result of close working relationship between Boeing and coating manufacturers, low VOC coatings have been added in several Boeing commercial airplane coating specifications as options to the conventional coatings. Use of these coatings is making significant contributions to the overall VOC emissions reduction in commercial airplane manufacturing and maintenance operations.

A. Corrosion Inhibiting Primer For Interior Fuselage Boeing Material Standard (BMS) 10-11, Type I

From the 1970's to the mid 1980's, little progress was made in low VOC coatings development throughout the commercial airplane industry. By the mid to late 1980's, a major effort was undertaken by Boeing and aerospace paint manufacturers as technology advancements were emerging. Also, technology driving regulations, such as South Coast Air Quality Management District (SCAQMD) Rule 1124, were being promulgated establishing future dates for lower VOC primers. All state-of-the-art low VOC primers such as water based, exempt solvent (1,1,1-TCA) based and high solids technologies from coating manufacturers were evaluated. By late 1987, only exempt solvent based primers could meet the regulatory and stringent performance requirements in film thickness, drying time, adhesion, humidity, hydraulic fluid and corrosion resistance required by BMS10-11. Two exempt solvent based primers were added to the Qualified Products List (QPL) as BMS10-11 Type I, Class A, Grade B primers. These exempt solvent based primers, while compliant with Rule 1124, contain large amounts of non-photochemically reactive methyl chloroform. Methyl chloroform has been identified as an upper atmosphere ozone depletor and its production will be phased out prior to 1996 in accordance with the Montreal Protocol. In light of this, the implementation of the exempt solvent based primers was regarded as an interim solution. Development work, in conjunction with Deft Chemical Coatings, continued toward development of a hydraulic fluid resistant version of its Mil-P-85582 water reducible primer. After 5 years of extensive effort a product was qualified and added to the QPL as BMS10-11, Type I, Class A, Grade E.

Table II shows the major property differences between the BMS10-11, Type I, Grade A (conventional), Grade B (exempt solvent) and Grade E (water reducible) primers. Figure I shows the rapid viscosity increase of Grade E primer after 4 hours at 75 F. Use of refrigeration to chill the mixed Grade E primer to below room temperature (above 50 F) has been demonstrated to be a viable way of obtaining longer pot life. Boeing controls allow for only 9 months shelf life as compared to 24 months for Grade A primer demonstrating that these primers are less stable dispersions than conventional primers.

TABLE 1, LOW VOC PRIMERS AND TOPCOATS EVALUATED SINCE 1985

	LOW VOC TECHNOLOGY						
1/SPECIFICATION	TYPE	<u>TCA</u>	M1-SOL	WATER	E-COAT	POWDER	TOTAL
BMS 10-11, TYPE I	PRIMER	50	33	37	2	0	122
BMS 10-79 TYPES II&III	PRIMER	7	19	12	0	0	38
BMS 10-11, TYPE II	ENAMEL	1	62	1	Q	5	69
BMS 10-60, TYPE I	ENAMEL	0	5	0	0	0	5
BMS 10-60, TYPE II	ENAMEL	0	40	0	0	0	40
CHROMATE FREE	PRIMER	2	13	4	0	0	19
BMS 10-86	ENAMEL	0	5	0	0	0	5
BMS 10-83	ENAMEL	0	6	2	0	0	8
BMS 10-20	PRIMER	0	3	4	0	0	7

1/ DESCRIPTIONS OF SPECIFICATION DESIGNATIONS

BMS10-11, Type I	Chemical and solvent resistant epoxy primer
BMS10-79, Types II & III	Urethane compatible, corrosion resistant primer
BMS10-11, Type II	Chemical and solvent resistant epoxy enamel
BMS10-60, Type I	Exterior protective enamel for general use
BHS10-60, Type II	Exterior protective enamel possessing a high degree of flexibility for specific use
BMS10-86	Teflon filled coating
BMS10-83	Interior decorative urethane paint system
BMS10-20	Corrosion resistant finish for integral fuel tanks

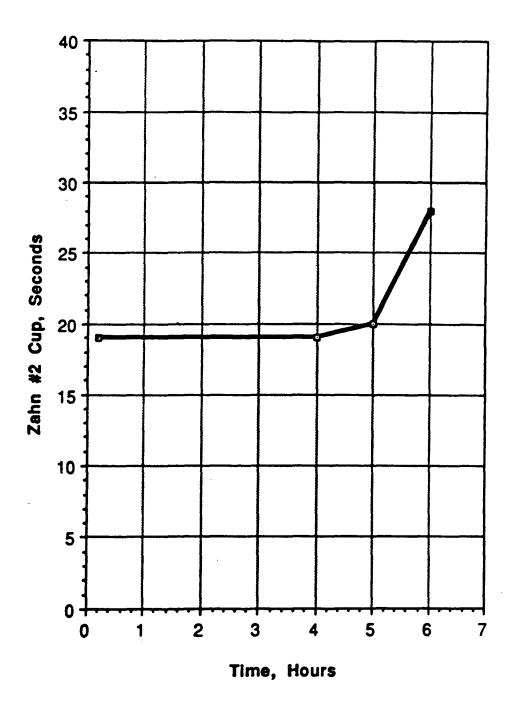


FIGURE 1. DEFT 44GN11 VISCOSITY PROFILE at 75F

Table II, Differences Between Low VOC and Conventional Primers for Interior Fuselage Application

BMS10-11,Type I Primer, Grade	A, (Typical)	B, (DeSoto)	B, (Akzo)	E, (Deft)
% N.V., Admixed	38.0	39.9	32.7	35.0
VOC, g/liter	Less than 650	Less than 350 (Excluding 1,1,1-TCA)	Less than 350 (Excluding 1,1,1-TCA)	Less than 350
Viscosity, Secs. No. 2 Zahn	15-17	14-17	15-17	18-22
Dry-to-dust, Mins.	5	15	15	10
Pot Life, Hours (At 75 F)	16	6	16	4
Shelf Life, Months	24	9	9	9

One of the characteristics of the Deft water reducible primer is that it requires consecutive additions of three separate and equal quantities of water to the base/catalyst mix in order to obtain a proper dispersion. The so-called "waterborne" primers now being developed by other manufacturers include the water in either the base or catalyst or both and are mixed similar to the conventional primer. However, further development of this new waterborne primer technology will be necessary to meet commercial airplane primer specifications.

In addition to these technologies, efforts in high solids primer development are continuing. Recent submittals from suppliers have shown significant improvements in application, dry film thickness, dry time and pot life. Electrocoat primer candidates from PPG and Sherwin-Williams have also been investigated. Improvement in corrosion resistance and lower bake temperatures are needed to make electrocoating a viable option for priming commercial airplane components.

B. Corrosion Inhibitive Primer For Exterior Fuselage And Wing Areas (BMS10-79)

In conjunction with the SCAQMD Rule 1124 requirements, an exempt solvent based primer was added to the QPL of BMS10-79 as a Type II & III, Grade B primer in early 1988. Table III compares the major differences between the Grade A (conventional) and Grade B primers.

Table III. Differences Between BMS10-79 Grade A and B Primers

BMS10-79, Primer, Grade	A, (Type III Typical)	B, (DeSoto)
% N.V. Admixed	35.7	24.2
VOC, g/liter	Less than 650	Less than 350 (Excluding 1,1,1-TCA)
Viscosity, No. 2 Zahn, Secs.	15-17	12-16
Shelf Life, Months	12	9
Pot Life, Hours	8	6
Hydraulic Fluid, 30 days Immersion at 75F	HB <u>1</u> /	4B <u>1</u> /

1/ pencil hardness of coating following exposure

While evaluation of other potential low VOC BMS10-79 primers (waterborne and high solids) is continuing, the only low VOC material currently available is the Grade B primer.

C. Chemical Resistant Epoxy Enamels For Interior Fuselage (BMS10-11, Type II)

Boeing initiated efforts on both interior (BMS10-11, Type II) and exterior (BMS10-60) enamels for commercial airplanes since the mid 1988's. Technology driving regulations were being established. SCAQMD Rule 1124 established a 420 g/l requirement effectivity of July 1, 1991. Since film thickness and dry time parameter were not as stringent as with primers, the majority of the coatings from suppliers were high solids enamels which involved less drastic formulation changes as compared to other technologies. Two qualified low VOC high solids epoxy (less than 420 g/l) enamels were added to the QPL of BMS10-11 as Type II, Grade D enamels. These materials have application characteristics similar to the conventional Grade A coatings, however, they have shorter pot and shelf lives, longer dry times, and higher application viscosities as shown in Table IV. The Grade D enamels require only 15 minutes of induction time compared to the 1 hour required by the conventional Grade A enamels. This is probably due to the use of lower molecular weight (liquid) epoxy resins in high solids formulations, which helps to reduce the time for induction.

Several powder coatings were evaluated for qualification as an option to conventional BMS10-11, Type II enamels. Appearance (too much orange peel) and

the tight tolerance of 250 ± 5 F in bake were the main constraints in using these coatings. Efforts to improve appearance and lower the cure temperature by suppliers are continuing.

D. Exterior Protective Enamels For Wing And Fuselage Areas (BMS10-60, Type II)

High performance urethane enamels have been used as protective topcoats for the exterior areas of airplanes such as the fuselage and wing areas because of their superior weather and chemical resistance for many years. As in the case of interior enamel (BMS10-11, Type II), essentially all the low VOC submittals from suppliers were high solids (urethane) coatings (Table I). Two high solids urethane enamels have passed the qualification tests in specification BMS10-60. Table V shows these qualified enamels perform similarly to conventional solvent based DeSoto Series 1000 (BMS10-60, Type II, Grade A). Both DeSoto and Akzo low VOC products are listed in BMS 10-60 as Type II, Class B, Grade D enamels. Time and temperature cure cycles for these coatings are similar to those for conventional coatings. Work is continuing with suppliers on improved application properties for exterior fuselage applications and on lead-, cadmium-, and chrome-free tint lines for these low VOC enamels as well as a more hydraulic fluid resistant version (BMS10-60, Type I) of these topcoats for general use.

E. Teflon Filled, Abrasion Resistant Urethane Enamel For Wing Areas (BMS10-86)

For protection of the high erosion areas of the wings such as the leading edge and some of the high rub areas (e.g. flap tracks areas of the wings) of the commercial airplanes, a teflon filled, abrasion resistant urethane enamel (BMS10-86) is generally used. Low VOC (less than 420 grams/liter) teflon filled abrasion resistant urethane coatings from Crown Metro have been qualified to BMS 10-86 as Type I (sprayable) and Type II (brushable) Grade D enamels. These high solids urethane enamels have improved (significantly shorter) drying times compared to conventional Grade A coatings. With the high solids enamel, usually two coats will be sufficient to provide 5 to 10 mils film thickness required by BMS10-86 whereas, with the conventional Grade A enamel, 3 to 4 coats are required.

F. Additional Low VOC Paint Development Efforts For Commercial Airplanes

During the past several years, Boeing has also been evaluating both waterborne and high solids candidates for a variety of other coating types as shown below:

- o Corrosion resistant finish for integral fuel tank (BMS10-20)
- o Interior decorative urethane paint system (BMS10-83)
- o Nonchromate primer for nonmetallic composites (BMS10-103)
- o Flexible corrosion inhibiting coatings for in-spar areas of the wings (BMS10-100)
- o Nonchromate primer for metals

Table IV, Differences between BMS10-11, Type II, Grade A and D Enamels

BMS10-11, Type II, Class B, Grade	A, (Typical)	D, (Akzo 446-22 Series)	D, (Crown Metro 14F21 Series)
%N.V., Admixed	49.6	67.7	61.8
VOC, g/liter	Less than 600	Less than 420	Less than 420
Viscosity, Secs. Zahn No. 2	20-25	25	28
Pot Life, Hours	16	4	4
Shelf Life, Months	24	9	9
Induction Time, Hours	1	1/4	1/4
Dry Time, Hours, At 75 F Dust Free Tack Tree Dry Through	1/2 3 6	2 4 9	2 4 6
Dry-to-stack	8	9	7
Appearance	Control	Slight Orange Peel	Slight Orange Peel
Sag	None	None	Slight

Table V, High solids exterior protective urethane enamels

BMS10-60, Type II, Class B, Grade	A, (DeSoto Series 1000 Control)	D, (DeSoto Series 420)	D, (Akzo 646-88 Series)
%N.V., Admixed	54.8	65.95	64.71
VOC, g/liter	534	417	418
Viscosity, secs., Zahn No. 2	16-18	17-19	20-24
Shelf Life, Months	12	9	9

Table VI, Dry time and shelf life for BMS10-86 Grade D enamels

BMS10-86, Grade	A, (Typical)	D, (Crown Metro 23T3 &24T3 Series)
%N.V., Admixed	55.6	68.0
VOC, g/liter	500-590	Less than 420
Dust Free, Hours	Type I 2.0 Type II 2.0	Type I 1.5 Type II 0.75
Tack Free, Hours	Type I 6.0 Type II 4.0	Type I 3.25 Type II 2.0
Dry Through, Hours	Type I 12.0 Type II 6.0	Type I 5.25 Type II 3.1
Shelf Life, Months	12	9

Several low VOC technologies for BMS10-20, BMS10-83 and BMS10-103 are currently being evaluated. For flexible corrosion inhibiting coatings for in-spar wing areas (BMS10-100), high solids vinyl technology may be available from suppliers in the near future. However, the availability of a low VOC nonchromate primer for use on aluminum structures will at best, several years away. Current state-of-the-art nonchromate corrosion inhibitive pigments do not perform as well as chromate pigments in protecting adjacent scratched or damaged (uncoated) areas. Corrosion pit depths of 1 to 10 mils have been observed in scribed areas on 2024-T3 bare aluminum panels coated with primers containing nonchromate inhibitors after 3000 hours salt spray exposure³. This is quite large when compared to attack observed with conventional chromated primers, which ranges from 0 to 0.1 mils depth. Boeing is also evaluating potential corrosion inhibitors using electrochemical polarographic and impedance techniques. If a suitable inhibitor is identified, cooperative efforts with coating suppliers to develop an acceptable primer will follow.

CONCLUSION

Significant progress has been made by the joint efforts of the Boeing Company and its coating suppliers in development of low VOC primers and enamels for commercial airplane paint operations. Since 1985, over 300 different state-of-the-art low VOC primer and enamel formulations have been tested. As a result of this effort, several low VOC coatings have been developed and qualified. This is allowing Boeing and its subcontractors to significantly reduce VOC emissions from painting operations. Based on EPA paint usage and emissions estimates for commercial aerospace painting operations, it is estimated that use of the materials developed to date will provide approximately a 40% reduction in paint emissions by Boeing and its subcontractors.

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- 2. Albers, R. A., U.S. Patent 4,352,898, "Water-Reducible Epoxy Coating Compositions Without Emulsifier", October 5, 1982.
- 3. "Salt Spray (fog) Testing", Boeing Specification Support Standard BSS 7249, Aug. 22, 1988.

SESSION 10

AUXILIARY SYSTEMS

PAPERS PRESENTED:

"Low Volatility Surface Preparation: A Hybrid Approach"

by

Joseph A. Lucas

Inland Technology, Inc.

Tacoma, Washington

"Transfer Efficiency and VOC Emissions of Spray Gun and Coating Technologies in Wood Finishing"

b

Lesley Snowden-Swan

Pacific Northwest Laboratory

Richland, Washington

and

Pamela Worner

Pacific Northwest Pollution Prevention Research Center

Seattle, Washington

"You Can't Always Judge a Paint Spray Gun Cleaning System by Its Cover"

by

Michael J. Callahan

Project Engineer

John P. Kusz

Manager of Product Development

Safety-Kleen Corporation

Elgin, Illinois

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

LOW VOLATILITY SURFACE PREPARATION: A HYBRID APPROACH

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In the past, industrial surface preparation practices have generally involved some variant of the following solvent usages:

- 1. Manual wiping with MEK, MIBK, Lacquer Thinner, Acetone, 1,1,1 Trichloroethane, Freon 113, Methylene Chloride, Xylene, Toluene, or Mineral Spirits.
- 2. Agitated dips or sprays using many of the above compounds.
- 3. Vapor degreasing using Freon 113, 1,1,1 Trichloroethane, Trichloroethylene or Perchloroethylene.

These materials and methods have worked well for industry as surface preparation techniques, primarily because they have grown up with industry during the last 50 or so years. As a new industrial cleaning need was identified, a selection of these solvents was empirically tested by the users; and, when one was determined to work effectively, it was adopted into the process.

In fact these traditional solvents were so effective, in terms of cleaning efficiency and economy, they were nearly "no brainer solvents". In other words one could literally specify "vapor degrease with 1,1,1 Trichloroethane" without knowing how clean that makes a surface, knowing how effective it was at removing specific contaminants, or knowing anything about the follow-on requirements, and still be fairly certain everything would work. They could be certain that the weld would perform, the paint would adhere, and the adhesives would bond.

Now, with the effects of The Clean Air Act, the Montreal Protocol phase out, the V.O.C. labeling requirements, and VOC limitations from a variety of sources looming imminent, these traditional industrial solvents are under major attack; and their continued use in industrial processes are becoming a major disadvantage for all industrial users.

This has, in the last two years, created a major push to discover and develop alternative chemistries, and alternative processes, to accomplish the same surface preparation tasks without incurring the same regulatory pressure and without causing the same risks to the environment and human health.

Contrary to the "No Brainer" characteristics of the traditional surface preparation techniques, alternate chemistries and processes are by no means as universally effective. In fact they tend to be extremely application specific. For example, a major aircraft manufacturer used MEK to prep prior to painting, sealing, bonding, and welding. It also used MEK to remove adhesive, remove cured sealant, remove DyChem layout dye to remove part marks, and for cleaning painting equipment. The low VOC surface preparation that was developed to prep prior to painting, bonding, sealing or welding works well for those applications but will not remove DyChem dye part marks, cured sealant or protective wing coatings. A different substitute was developed that removes DyChem dye, cleans paint equipment, and removes some adhesives, however it will not prep surfaces, remove cured sealant, or remove protective wing coatings. A third substitute that will remove cured sealant and adhesives will not prep surfaces or remove protective wing coatings. Protective wing coatings must be removed by means of yet a fourth material.

To add to this complexity there is very little existing information or data regarding the cleanliness requirements for any of the typical industrial follow-on processes. This naturally means that there is no way to effectively compare cleanliness results achieved via a potential substitute against a known requirement. This lack of data within industry continually raises the specter of the unknown. Will the weld hold as good, will the paint bond as well, will the circuit board last 20 years, or will some unobserved or unknown difference in the process put the company's product and reputation in jeopardy? This lack of good, replicable, comparable test data is probably the primary impediment to the efficient design and adoption of low VOC chemistries and processes, a more complete list of impediments is as follows:

- 1 Research chic
- 2. Research and design first, find application second
- 3. Desire for quick fix that behaves like the old stuff
- 4 We tried that before and it didn't work
- 5. No involvement of line workers
- 6. Unwilling to look at process changes and equipment changes
- 7. Fear of unknown effects of new materials
- 8. Lack of management courage
- 9. Lack of real data about processes. Is this chemical really necessary?
- 10. Failure to look upstream for changes that may make a chemical unnecessary
- 11. Unwilling to make employees accept the need to change
- 12. Desire for substitution of a product and/or process that is already validated, reluctance to do on site testing and adaptation.
- 13. Establishing substitution criteria that pre-ordains failure. The substitute must:
 - A. Be non-flammable
 - B. Be non-toxic
 - C. Be non-regulated
 - D. Work with minimal process changes
 - E. Be cheap!

- 14. Lack of real technical knowledge about the current process
- 15. Lack of real technical data about the proposed alternative chemical/process. How clean does this get and is that good enough?

Some of these impediments can be ameliorated by shifting the attention away from the seductive tendency to focus on the solvent that is to be eliminated. Currently the cry is "I want a replacement for 1,1,1 Trichloroethane". This focus is usually of limited productivity because of the lack of process information. Was 1,1,1 Trichloroethane being used because it alone would remove the particular contaminants sufficiently for the follow-on process or was it being used because it worked? Was its use in essence the result of industrial habit?

The most productive focus in designing or trying to identify a substitute is to focus on the application for which the current solvent is being used. What must be accomplished in order for the follow-on process to work?

The following is a helpful diagnostic protocol that is designed to aid in deriving the necessary data from the industrial solvent usage process:

- 1. What is the solvent being substituted? Why is this particular solvent being used for this process?
- 2. What is the motivation for this substitution?
- 3. What is the process the solvent is being used in? Manual wipe, vapor degreaser, ultra sound, etc.
- 4. What is the substrate?
- 5. What are the contaminants that are being removed? What is their origin?
- 6. What are the follow-on processes? Do they require this cleaning step?
- 7. How clean do you need the surface to be for the follow-on process?
- 8. Are there any contra-indications? (i.e. sulfur with aluminum at high temperatures)
- 9. Have you tried anything else as a substitute? What was it? What were the reasons for its non-acceptance?

Over the course of the last several years, we at Inland Technology have not only been developing data on the performance of our products, but we have been collecting quality data on the cleaning performance of many of the traditional solvents. Researchers have used a wide variety of test methodologies and measuring equipment. Much of the test results are not comparable in any meaningful way between methods, however this information, sketchy though it may be, should be the beginning of a useful base line of performance data that will enable industry, by using identical test methodologies, to begin comparing the performance of substitute chemistries and processes.

The following is test data comparing the performance of traditional solvents with Inland Technology alternatives:

OSEE TEST

Traditional Solvent 1,1,1 Trichloroethane	Delta cV	-135
Inland Technology Alternative Citra Safe®	Delta cV	-32.2

On OSEE tests the smaller the Delta cV either positive or negative the cleaner the surface.

NVR TEST

Traditional Solvent 1,1,1 Trichloroethane	MG/Plate 8"x12"	1.0-1.47
Inland Technology Alternative Citra Safe®		1.73

X-RAY FLUORESCENCE

Traditional Solvent Isopropyl Alcohol	4 Counts/Second
Traditional Solvent Freon TE	ND (non detectable)
Inland Technology Alternative Citra Safe®	2 Counts/Second
Inland Technology Alternative Skysol 500	ND (non detectable)
Control Uncleaned Aluminum	301 Counts/Second

OPTICAL SCANNING TEST

	Inland Technology Alternatives Outperforming Freon T.E.
Traditional Solvent Freon T.E.	EP 921
	X-CALIBER
<u> </u>	CITRA SAFE®

Expanding on this small beginning by developing on this base of test data should help take the development and adoption of alternative surface preparation chemistries and processes out of the frustrating, risky, labor intensive realm it currently occupies, and through the development and use of scientific performance data, put this process firmly into the less stressful engineering realm where it belongs.

To date most of the chemical design work in the low VOC substitute arena has focused on the following aqueous, semi-aqueous, and hydrocarbon cleaning chemistries. These approaches have several inherent disadvantages that have impeded their universal adoption.

DISADVANTAGES OF AQUEOUS CLEANING

- 1. Typically does not lend itself to manual surface cleaning
- 2. Parts with blind holes and small crevices may be difficult to clean and require expensive process optimization

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- 3. Less effective on non-polar soils than polar
- 4. Potential for galvanic corrosion to occur during process
- 5. Some materials and processes are incompatible with water
- 6. Higher energy consumption
- 7. Rinsing difficulties-Some surfactants and other components can be difficult to rinse
- 8. Sometimes high concentrations of organic coupling compounds contribute to organic emissions.
- 9. Process equipment tends to be large and requires considerable space.

DISADVANTAGES OF SEMI-AQUEOUS CLEANING

- 1. Typically does not lend itself to manual surface cleaning
- 2. Flammability especially if sprayed
- 3. Odors
- 4. High hydrocarbon content (terpenes etc.) can auto-oxidize in the presence of heat, water, and air to increase non-volatile residue problems
- 5. Sometimes the surfactants are difficult to rinse
- 6. The chemistry of maintaining proper emulsion characteristics during the process can be difficult
- 7. Higher organic concentrations can lead to higher organic emissions.

DISADVANTAGES OF STRAIGHT HYDROCARBON CLEANING

- 1. Flammability Problems
- 2. Typically 100% VOC
- 3. The need for low non-volatile residue tends to require the use of lower flash point lighter fractions that evaporate rapidly and contribute massively to organic emissions
- 4. Low-volatility hydrocarbons typically leave objectionable residue unless extremely purified to include only one hydrocarbon chain
- 5. Typically not effective on all soils

6. Contaminate build-up in the cleaning tank can quickly cause a failure of the follow-on process

HYBRID CHEMISTRIES

As a result of the difficulty experienced in attempting to replace the Ozone depleting substances and other traditional highly volatile solvents, with more benign chemistries following the approaches of aqueous, semi-aqueous, and hydrocarbon technologies, Inland Technology Incorporated has developed a new hybrid approach, that from preliminary test data, promises to solve many of the inherent problems associated with the other three approaches (Aqueous, Semi-Aqueous and Hydrocarbon cleaning systems). This for lack of a better term is being referred to as "Hybrid Chemistry".

In many respects this Hybrid Chemistry incorporates many of the advantages of Aqueous, Semi-Aqueous and Hydrocarbon cleaning systems while eliminating or markedly reducing many of their inherent disadvantages.

These modified hydrocarbon systems provide aggressive removal of a wide range of contaminants. Components with large differences in inter-molecular forces of non-polar dispersion, polarity, and hydrogen bonding are combined together to optimize contaminant solubility. On the molecular level this means that components with the greatest affinity to the contaminant tend to dominate the surface interface between the liquid and the contaminant; that component is also most likely to solubilize the contaminant. As a result, one blend might provide the characteristics necessary to remove several very different contaminants. Hydrophobic contaminants are attracted by the high dispersion, low polarity, and low hydrogen bonding components of the system. Various "modified" hydrocarbons - oxygenated, nitrogenated, but not halogenated - are used to attack polar, and hydrogen bound contaminants. Coupling agents are present to facilitate rinsing and solubilizing of all the materials including the contaminant.

ADVANTAGES OF HYBRID CHEMISTRIES

- Can be designed to be nearly or essentially non-volatile.
- Even though they may be non-volatile, hybrids can be designed to be extremely free rinsing.
- Hybrids can have extremely high flash points.
- Hybrids can contain design components that exhibit strong polarity, strong dispersion forces and strong hydrogen bonding characteristics to enable one cleaning agent to be effective on a wide variety of contaminants.
- Hybrids exhibit a high capacity for contaminant loading while maintaining specified cleaning requirements.
- Hybrid chemistry is capable of delivering the exquisitely clean surfaces mandated by the most demanding of precision cleaning requirements.

Several such hybrid systems have been designed by Inland. Most of the components of our hybrid systems originated from usage in industries such as the food industry and cosmetics industry. All have relatively high flash points, extremely low vapor pressures, and provide a major improvement in human and environmental safety. Three of the products are CITREX, X-CALIBER, and EP 921.

X-CALIBER

This product is designed to replace TCA, TCE and Methylene Chloride as a surface prep and stripper. It is used as an in-tank solution substitute for vapor degreasing with TCA, TCE or Freon. It is also used for paint and coating stripping as a substitute for Methylene Chloride. X-CALIBER has the ability to aggressively remove and suspend both polar and non-polar contaminants.

Highly polar at the same time with strong London forces of dispersion, X-CALIBER attacks a wide variety of contaminants. Its hybrid nature tends to keep contaminants mobilized thereby reducing the effects of contaminant build-up in the tank. This characteristic is a major technical improvement over most straight hydrocarbon or aqueous/semi-aqueous cleaning chemistries.

CITREX

CITREX has many of the same characteristics as X-Caliber, but it is less aggressive and has a lower surface tension. It is another in-tank substitute for vapor degreasing and also stripping procedures. It is slightly less aggressive than X-Caliber, but it does have a higher flash point (142 °F), CITREX wets most surfaces better than X-Caliber and is more easily rinsed with water.

EP 921

EP-921 is a design effort to tame the hybrids sufficiently to allow for their use as hand applied wipes for surface preparation prior to painting and other follow-on processes. Like all of the hybrids, a follow-up rinse or wipe is required as a standard process to achieve the low N. V. R., of which they are capable. In the case of EP-921, a simple rewiping of the surface with a rag dampened with water has proven sufficient for most follow-on processes.

While X-CALIBER and CITREX more nearly substitute for TCA & TCE, EP-921 was designed chemically to more nearly mimic the behaviors and characteristics of Methyl Ethyl Ketone.

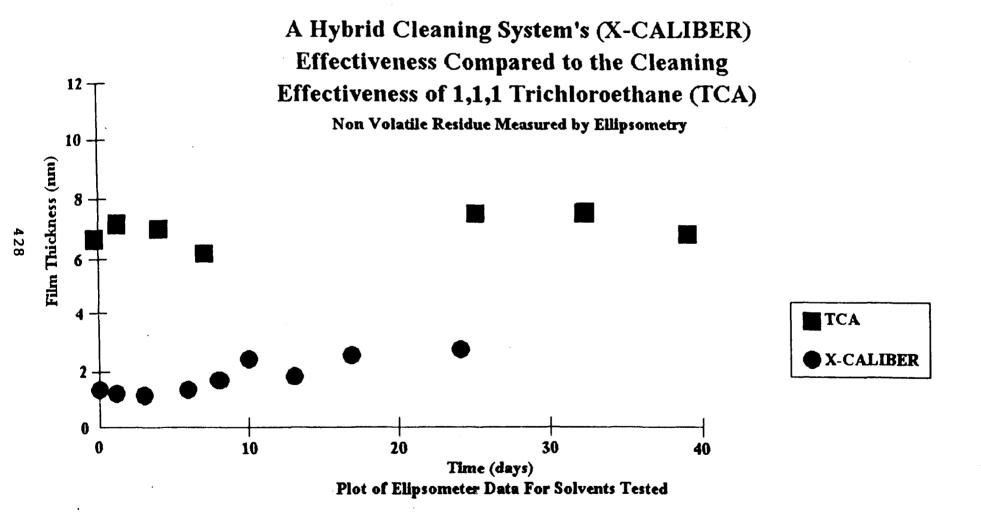
This led to the discovery of a new application for this extremely low volatility solvent substitute. Although 25 - 30% of solvent emissions in coating related activities come from surface preparation, another, nearly equal, 25% is related to paint equipment clean up.

EP-921 is a low volatility substitute for MEK and is effective at thinning and mobilizing most of the paints and coatings it has been tested against. Guns, pots, etc. clean up with the same effort, the same equipment, and the same techniques as with using MEK.

The major advantages are: a vapor pressure of <.1 M M H G instead of 75 M M H G.

This makes EP-921 750 times less volatile than M.E.K.

EP-921 has a flash point of 146 °F - rather than the 20 °F flash point of M.E.K. and has a much more benign toxicology for worker safety.



SOLVENT SUBSTITUTION

CASE STUDY

CLIENT:

The Boeing Company

PROJECT:

Eliminate or severely reduce the use of the Methyl Ethyl Ketone used for cleaning paint guns & painting equipment used in aerospace coating applications. A successful substitute must be less hazardous than MEK and must fit within the VOC regulations promulgated by PSAPCA and SCAQMD.

CONCERNS:

The project raised three major areas of concern:

- 1. VOC regulations demand near non-volatility in paint gun cleaning materials. This lack of volatility raised possible contamination issues with regards to painting subsequent to cleaning with substitutes.
- 2. Most paint equipment is designed to be resistant to MEK. There will be very little data available regarding component resistance to any substitutes.
- 3. There are a great variety of coating systems in use today. The goal of the project was to create a substitute with the near universal applicability of MEK.

SUBSTITUTION PROCESS:

1 Try to create on a macro scale a material that mimics some of the electro chemical characteristics of MEK.

- 2. Keep the vapor pressure below .5 mmHg & the volatile content below 200 grams per liter.
- 3. Test candidates on as many paint & coating systems as possible.
- 4. Devise & test purging techniques to eliminate paint contamination questions.

METHODOLOGY:

The final candidate was a cleaning formulation identified as EP921. This material was constructed from mutually antagonistic materials that as a whole mimic, on a macro scale, the solubility parameters & the solubility vector enjoyed by Methyl Ethyl Ketone.

Its near non-volatility would allow it to compete effectively, in terms of emissions, with MEK coupled with a vapor capture system of 99.7% efficiency.

Cleaning effectiveness equal to MEK on 1011 Epoxy Primer, 1060 Series Topcoat, iron, alkyd enamels, varnish, polyeurothanes, & silicone coatings.

Residue concerns have been eliminated by the successful use of a warm water final rinse of the paint gun. This is then followed by an air blast to dry the gun prior to use.

Testing on paint gun components to date has not resulted in identifying any material adverse effects.

RESULTS:

The client is continuing testing & initiating Boeing Material Technology materials testing prior to developing specifications for use. Northrop Aviation has also conducted tests & has received preliminary approval from SCAQMD and PSAPCA. Evaluation regarding Aerospace VOC regulations

is in process. The original client is experimenting with other applications for this mimic of MEK.

To date, good preliminary results have been obtained in the following traditional MEK applications:

- Felt marker remover
- Removal of glues & adhesives
- Mild paint remover
- Grease & oil remover
- Machinists blue dye removal

Inland Technology Incorporated

Inland Technology Incorporated, is a privately owned corporation that is dedicated to the development and production of advanced solvents that are critical to all industries having to respond to the environmental challenges of the 1990s. Inland, operating from their facilities in Tacoma, Washington, is committed to customer satisfaction through quality - Total Quality Management (TQM) is an essential component of Inland's corporate commitments. During the past eight years, Inland has become a preeminent company in the advancement of environmentally responsive solvents:

- Inland is a member of the Joint Association for the Advancement of Supercritical Technology (JAAST). Inland was invited to participate as a full member amongst other technology giants such as Los Alamos National Laboratories, Battelle Northwest Laboratories, IBM, Boeing, Hughes and Autoclave Engineering.
- Inland is an invited member of International Air Transport Association and participated in their subcommittee for non chlorinated paint stripping alternatives.
- Inland is active in the ASTM G-4 subcommittee searching for new technologies for cleaning LOX lines.
- Inland is active in the SAEG-9 subcommittee on advanced methods for sealant applications
- Inland is an invited participant on U.S. Environmental Protection Agency's "Use Cluster" committees for development of printing and aerospace industry regulations.

Inland actively supports many of the largest companies in the United States, as well as federal government agencies, including: Westinghouse, Weyerhaeuser, Kodak, McDonnell Douglas, Grumman, Northrop, Boeing, Los Alamos National Laboratories, Lawrence Livermore National Laboratory, U.S. Navy, and the U.S. Air Force.

TO DATE, THE SCIENTISTS AND ENGINEERS AT INLAND TECHNOLOGY INC. HAVE DEVELOPED SUCCESSFUL SUBSTITUTES FOR THE FOLLOWING PROBLEM SOLVENTS:

DOXIC SOLVENT	rexëe	SUBSTRUTTES	GOMMENTS
Methylene Chloride	Paint stripping; cold tank soak; resin removal	CITREX X-CALIBER	Both products are biodegradable; CITREX is not regulated by RCRA or SARA, Title III. Both are low VOC.
1,1,1 Trichloroethane	Electronic & electrical cleaning. Also, metal preparation	CITRA SAFE® TEKSOL EP	CITRA SAFE is biodegradable; TEKSOL EP is not regulated by SARA, Title III. Both are low VOC and non chlorinated
Methyl Ethyl Ketone (MEK)	Surface preparation for painting or welding	SAFETY PREP CITRA SAFE TEKSOL EP	SAFETY PREP, CITRA SAFE and TEKSOL EP are biodegradable, all are low VOC's
Toluene / Xylene	Surface preparation for painting or welding	SAFETY PREP CITRA SAFE TEKSOL EP	Same as above
Acetone	Cleaning of fiberglass & epoxy resins	Z-STRIP CITREX	Low VOC's & toxicity; High flash point; CITREX is biodegradable
Stoddard Solvent / Mineral Spirits	Parts washing & paint clean up	CITRA SAFE TEKSOL EP BREAKTHROUGH	Low VOC's; CITRA SAFE is biodegradable; BREAKTHROUGH is free from most regulations TEKSOL EP is low toxicity
Trichloroethylene	Degreasing & resin removal	CITREX TEKSOL EP CITRA SAFE	CITREX and CITRA SAFE are biodegradable, low VOC. TEKSOL EP is non chlorinated with low toxicity
Perchloroethylene	Degreasing	CITRA SAFE ISO-PREP BREAKTHROUGH	Non-halogenated Low VOC's, easier disposal; Low Toxicity
Methyl Ethyl Ketone (MEK)	Paint Gun Cleanup	EP 921	Biodegradable, High Flash Point, Low VOC, not regulated by RCRA or SARA Title III
Freon 113	Vapor Degreasing; Precision Cleaning	CITRA SAFE OR SKYSOL WITH ULTRA FILTRATION	CITRA SAFE biodegradable; SKYSOL is not regulated by RCRA or SARA Title III, Section 313, both are low VOC's
1,1,1 Trichloroethane	Vapor Degreasing; Precision Cleaning	CITRA SAFE OR SKYSOL WITH ULTRA FILTRATION	CITRA SAFE is biodegradable; SKYSOL is not regulated by RCRA or SARA Title III, Section 313, Both are low VOC's

It should be noted that performance needs vary from application to application and that none of these substitutes should be expected to be 100% cross over for all applications.

Also, the chemical behaviors of these substitutes (vapor pressures, dry time, etc.) may differ from solvents being replaced which may require changes in work practices in order for substitutes to be successful.

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

TRANSFER EFFICIENCY AND VOC EMISSIONS OF SPRAY GUN AND COATING TECHNOLOGIES IN WOOD FINISHING

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SUMMARY

This study was designed to determine which factors most strongly influence net volatile organic compound (VOC) emissions and transfer efficiency (TE) of a spray coating operation in a "real-life" wood finishing environment. Factors tested included spray equipment types and coating types, as well as painter skill level and target size and shape. Transfer efficiency and coating usage were measured to rate the overall system performance (coating type plus application method) in an operating wood finishing shop. The equipment was designed to be representative of small- to medium-sized businesses in the wood finishing industry.

The study was not designed to determine the maximum achievable transfer efficiency for the various spray guns, but rather to provide a non-biased test of "off-the-shelf" equipment not optimized with variable tips. Spray time was included in the data in order to aid in the analysis of possible effects of the variables on production rate. The study showed that a painting operation must be viewed as a system, with gun type, coating composition, and especially painter skill all affecting environmental performance. The results also indicated that water-borne coatings may hold significant long-term potential for VOC reductions in wood finishing, and that painter skill level also exerts a strong influence on both transfer efficiency and VOC emissions.

INTRODUCTION

Improving transfer efficiency (TE) in spray coating operations would reduce coating waste and VOC emissions, cut hazardous waste disposal fees and coating costs, and lessen worker exposure to potentially hazardous materials. Changing from 30 percent transfer-efficient equipment to 65 percent transfer-efficient equipment would reduce materials usage by approximately 50 percent. Many factors affect achievable TE, including spray equipment type, size and geometry of the target, coating type, skill level of the spray operator, air velocity, atomizing air pressure, fluid flow rate, and fan size.

In this study, the impact of several factors which can affect achievable TE were investigated, including spray equipment type, size and geometry of the target, solids content of the coating, and skill level of the operator. Transfer efficiency and VOC emissions were calculated for each of these factors. Other factors which may affect TE, such as air velocity, atomizing air pressure, and fluid flow were monitored and kept as stable as possible for the duration of the spraying procedures. Environmental impact is clearly shown by the data on net VOC emissions, expressed in pounds of VOC per pound of solid applied, since those figures reflect both transfer efficiency and VOC content of the coating.

METHODOLOGY

Testing Environment

Spraying was conducted inside a concrete dry filter spray booth of dimensions 14' x 43 x 94' at a wood finishing facility in the Puget Sound area. Fresh dry filters were installed in the booth prior to testing. The average temperature, percent humidity and air velocity in the booth for the duration of testing were 70F, 65 percent, and 180 ft/min, respectively.

Operator Skill Level

To determine the importance of the human application factor on spray efficiency, the tests were performed with both a very experienced painter (over ten years spray painting experience) and a painter with limited experience (less than one year). The experienced sprayer had substantial experience with all of the spray guns tested. The novice sprayer had used all of the guns at least once; however, the bulk of his experience was with the HVLP air-assisted and HVLP equipment.

Target Size and Geometry

To investigate the effects of target configuration on transfer efficiency, two types of targets (door panels and cabinet face frames) were sprayed for each set of equipment and coating type used. The door panels provided a large flat target surface, while the frames offered a more complex shape. The door panels used were standard sized mahogany doors (dimensions 28" x 80", with a thickness of 1 3/8"). The simulated cabinet face frames were approximately 18" by 30", constructed from 2 1/4" x 1/2" hemlock door casings.

Coating Type

The physical properties of each coating type are listed in Appendix A, Table A.1. Each coating type consisted of a stain, a sealer, and a topcoat. A single brand of stain was used for all tests. Stain usage was measured for the initial tests. However, because the weight of stain used was negligible compared to the weight of the sealer and topcoat, stain usage was found to have no measurable effect on the calculated TE of the total coating system. Therefore, although stain was applied in the remainder of the tests, stain usage was not included in the transfer efficiency determination.

The 25 percent solids and 30 percent solids alkyd modified nitrocellulose lacquer are solvent-based coatings which are cured through the normal evaporative process to remove the

solvent. This type of coating is generally not available in a low-VOC material². Spraying was also conducted with the 30 percent solids sealer combined with a 40 percent solids alkyd/urea conversion varnish for the topcoat. This latter material contains a catalyst which promotes curing through a polymer crosslinking process. Though this type of coating is generally available in high solids (low VOC) content, the shelf life of the final mixed material (catalyst plus varnish) is less than one day, and thus good planning and management is required to avoid wasting material.

The third type of coating investigated is a self-seal acrylic emulsion water-borne lacquer (32 percent solids). While the use of water-borne coatings substantially reduces VOC emissions, these coatings generally require longer drying times compared to solvent-reducible materials, and generally require a heated environment, such as a curing oven. Despite these difficulties, water-borne coatings can be applicable to the wood finishing industry with some procedural modifications.

Spray Equipment Type

The spraying procedure used was modeled after regular production procedures used in the shop. Complete equipment specifications for the technologies chosen for testing is provided in Appendix A, Table A-2. The equipment tested was selected by spray gun and coating manufacturers' representatives participating in the study and are considered to be representative of technology available to small- to mid-sized wood finishing businesses.

The actual guns used in the study were newly purchased. In addition, the guns were used with the tips which were packaged with them, and no attempt to optimize gun performance by using variable tips was made. The guns were intentionally used in this manner to provide a flat comparison of "off-the-shelf" equipment.

Volume and Mass Measurement

Several measurements were necessary for the calculation of TE (see Appendix B, Equation B-1), including volume of coating used, mass of solids deposited on the target, weight percent solids, and density of the coating. The latter two measurements were also necessary for calculation of VOC content (see Appendix B, Equation B-4). The volume of coating material sprayed was measured using a fluid flow meter in conjunction with a pro-pulse receiver module. The mass of solids deposited on each target was determined by weighing the target before and after the coating system was applied using a Toledo SM30000 precision platform scale (+/- 0.1 gram).

Physical Properties Measurement

Coating samples were taken at the time of spraying and stored in sealed cans for later analysis in the laboratory. Percent solids, density, and viscosity were measured in a coatings laboratory. Weight percent solids was determined by weighing a designated quantity of coating specimen into an aluminum foil dish and heating at 200 degrees F to constant weight (approximately two hours). Density and viscosity measurements were made at the coating temperatures used for spraying using a weight-per-gallon cup and a Zahn #2 cup, respectively.

RESULTS

Transfer Efficiency

The transfer efficiency results vary widely. The maximum TE achieved in any of the tests approached 70 percent for the experienced sprayer and 60 percent for the novice sprayer, achieved both in spraying doors with the HVLP air-assisted gun and 30 percent solids coating system, and in spraying doors with the HVLP gun and water-borne system configurations (see Figure 1). The minimum TE achieved was 23 percent for the experienced sprayer when spraying frames with the conventional gun and 30 percent solids system, and 18 percent for the novice spraying frames with the HVLP-1 gun and 25% solids system. Due to the number of tests performed, it is difficult to determine immediately from these results the influence of individual factors such as gun type or coating on TE. It is most useful to consider each factor separately, as follows.

There is much concern and controversy within industry and the regulatory community regarding which spray gun technology gives the highest transfer efficiency. The EPA assumes a TE of 25 percent for conventional airspray, 40 percent for air-assisted airless, and 40 percent for airless spray (for the coating of metal parts). Although there is no universal TE assigned to HVLP, EPA region IX (San Francisco) assumes TE for HVLP to be greater than 65 percent (equivalent to electrostatic spray). Results from this study do not indicate a direct correlation between TE and spray gun type. Although individual guns did vary in TE, no one gun consistently outperformed another with all of the coatings used. In addition, the TE achieved by one gun varied by as much as 50 percent depending on the specific test configuration. Again, it should be noted that the spray equipment was not set up to give the optimum TE (i.e., with variable fluid tips and air caps), but rather were used off-the-shelf as received from the manufacturer. Pressures of fluid and air were, however, adjusted at the start of each test to ensure the best performance possible with the existing equipment.

Although transfer efficiency does appear to be affected by coating type, there is no clear trend regarding the relationship between percent solids and TE. Perhaps the most consistent factor seen to exert an influence on transfer efficiency is painter skill level. In 90 percent of the combinations tested, the expert sprayer achieved higher transfer efficiency than the novice. In fact, the differences in transfer efficiency due to painter skill level with a single gun type were often larger than differences between gun types. It is evident from these results that painter training and experience is a crucial factor in achieving optimal TE performance for spray coating operations.

Volatile Organic Compound (VOC) Emissions

A useful parameter for incorporating both the TE and VOC content of a coating application system is emissions (E). Emissions were calculated in this study as lb VOC/lb solids applied to the target (see Appendix B, Equation B.4). It is important to first notice the inverse relationship between TE and VOC emissions, i.e., with an increase in TE comes a decrease in VOC emissions. For example, spraying frames results in higher VOC emissions and lower TE, and the experienced sprayer consistently achieved lower emissions and higher TE than the novice.

The most significant influence on emissions, however, appears to be the actual VOC content of the coating material. Emissions appear to consistently decrease from the lower solids solvent-borne material to the higher solids material. In addition, tests run with water-borne coating show significantly lower emissions than all of the solvent-borne coatings.

Measurements of the amount of material of each coating type used to perform the spray operation were also taken. The results of these measurements demonstrate that, for each equipment configuration, the amount of water-borne coating material used was consistently lower than the solvent-based coating types. Obviously, reducing the amount of material used reduces the environmental impact of that material.

Spray Time

Although TE and VOC releases are perhaps the most important factors determining environmental performance of a spray painting system, an equally important consideration from an economics standpoint is production rate. If, for example, a particular spray gun technology offers high TE but decreases production, material cost benefits due to increased TE may suffer.

In order to provide insight into the possible effects of gun type on production rate, spray times were measured for each combination of spray gun and coating system. The average results of these times are shown in Figure 3. With regard to gun performance, airless application proved to be the quickest application method, while HVLP was the most time consuming. Once again, differences between the experienced and novice spray times clearly show the advantages of using a trained painter.

CONCLUSIONS

Strong conclusions regarding the effects of gun type on transfer efficiency or VOC emissions are difficult to draw from the data. However, a few important points regarding environmental effects in wood finishing operations are clear:

Painter skill level has a strong influence on achievable TE, VOC emissions, and spray time. This element of the system is a direct and simple measure for improving environmental performance. Training, both introductory and on-going, should include spray techniques, coating content, equipment set-up, and optimization.

Several factors work as a system to affect environmental performance. These include painter skill level, spray equipment type, and coating type, as well as uncontrollable factors, such as the geometry and size of the target. Solutions should be situation-specific, and all of the factors discussed above should be adjusted to optimize performance.

Waterborne coatings hold significant long-term potential for VOC reductions in wood finishing. As this study demonstrates, water-borne coatings provide significantly less VOC emissions as well as reduced materials usage, irrespective of spray equipment used. Operators are urged to request information on the latest in water-based materials from their vendors.

Figure 1. Transfer efficiency for all equipment types and coating systems (using data from expert painter spraying doors).

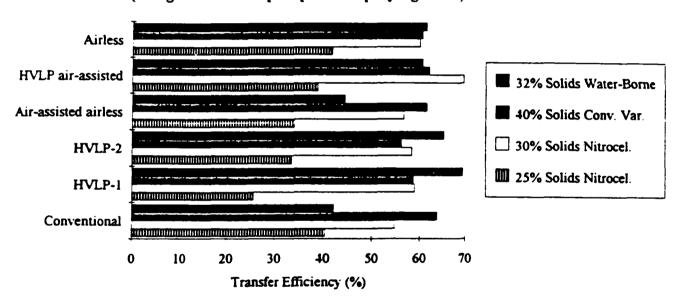


Figure 2. VOC emissions for all equipment configurations and coating types (using data from expert painter spraying doors).

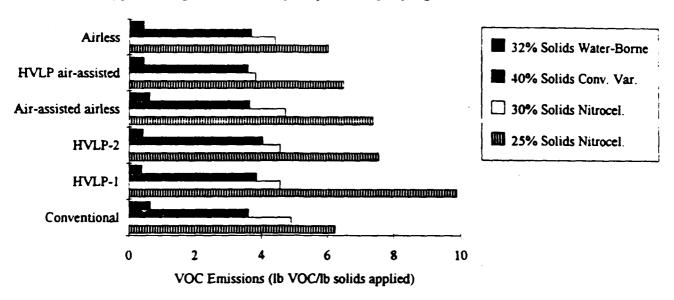
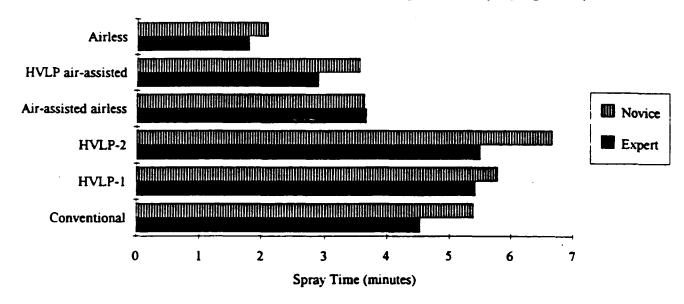


Figure 3. Spray time for expert and novice painters, with all equipment types (using average data from all coating systems, spraying doors).



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Appendix A Material and Equipment Specifications

Table A.1. Physical Properties of Coatings

Coating	Weight (% solids)	VOC (lb/gal)	Density (lb/gal)	Viscosity (Zahn, #2)
Sealer (25% solids)	26.07	5.73	7.74	33
Topcoat (25% solids)	29.72	5.36	7.62	45
Sealer (30% solids)	25.81	5.67	7.62	37
Topcoat (30% solids)	28.07	5.52	7.67	28
Conv. Varnish (40% solids)	35.79	5.17	8.06	33
Water-Borne (32% solids)	30.86	1.76	8.24	30

Table A.2. Spray Equipment Specifications

Gun Type	Conventional Airspray	HVLP-1	HVLP-2	Air-Assisted Airless	HVLP Air-Assisted	Airless
Manufacturer	Binks	Devilbiss	Accuspray	Graco	Graco	Graco
Model No.	2001	JGHV-530	#10	AA2000	AA2000	Silver
Serial No.		*****	3610155		******	
Air Cap	63PB	#28	#11	(standard)	222608	****
Fluid Tip	63B	0.0425 inch	0.051 inch	215/417*	215/417*	415/417*
Needle	563A	JGA402FX	0.051 inch	(standard)	(standard)	(standard)

First number represents fluid tip used for spraying face frames; second number is the tip used for doors

In addition to the spray guns and coatings described above, other equipment was needed to perform the tests. Pumps were used with the air-assisted airless and airless configurations (Graco, Model 10:1 Monark with 1/4 inch fluid and 3/8 inch air hoses and Model 30:1 president with 1/4 inch fluid hose, respectively). The fluid flow meter (Graco, CSA & FM approved; Class 1, Division 1, Model 224-222, Series F91A, Serial #C148) was used with a 200 mAmp power generator and a propulse receiver module. The fluid pressure pot (5 gallon ASME) included 1.4 inch fluid line and a 5/16 inch air line. Fluid temperature was measured with a thermometer (VWR Scientific Inc., 61014-020).

Appendix B Calculations

Transfer Efficiency. Transfer efficiency was determined on a mass basis using guidelines from ASTM Method D5009-89:

Equation B. 1

 $TE = (100 \times P) \times 100 / (F \times d \times S)$

where:

TE = transfer efficiency (%)

P = mass of coating solids deposited on target (g)

F = volume of fluid delivered (ml) d = density of coating (g/ml)

S = wt% solids of coating

Volatile Organic Compound (VOC) Content. VOC content was calculated using guidelines from ASTM Method D3960-90:

For solvent-borne coatings,

Equation B.2:

 $V_{a} = (100 - (S + X)) \times d \times 10$

where

V = total VOC content (g/l) (organic volatiles)

S = wt% solids of coating

X = wt% exempt solvent of coating

d = density of coating (g/ml)

For water-borne coatings,

Equation B.3:

 $V_{xx} = (V_x \times 100 \times d_x) / (100 - (d \times W))$

where

 V_{sw} = total VOC content (g/l), based on coating excluding water

V = total VOC content (g/l), determined from calculation B.2

 $d_{-} = 0.997$ g/ml (density of water at 25°C)

d = density of coating (g/ml)

W = wt% water of coating

Coating density (d) and percent solids (S) were determined in the laboratory (see Appendix A, Table A.1), while water content (W) was taken from manufacturers' coating specifications.

VOC Emissions. Emissions for each sealer + topcoat system were calculated with variables used in the above equations (assumes 100% of VOC content in coating material is dispersed into air):

Equation B.4:

$$E = \{(V_{\alpha} \times VOL_{\beta}) + (V_{\alpha} \times VOL_{\beta})\} / P$$

where

E = VOC emissions for sealer + topcoat (g VOC/g solids applied)

 $V_{\underline{z}} = VOC$ content of sealer (g/l)

 $V_{\perp} = VOC$ content of topcoat (g/l)

VOL = total volume of sealer used to finish target (1)

VOL = total volume of topcoat used to finish target (1)

P = mass of coating solids deposited on target (g).

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

YOU CAN'T ALWAYS JUDGE A PAINT SPRAY GUN CLEANING SYSTEM BY ITS COVER

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INTRODUCTION

The reduction of VOC emissions from surface coating not only applies to surface preparation and application, but to application equipment clean-up as well. Specifically, most paint spray gun cleaning systems use VOC's for cleaning and, therefore, are another emission source which must be evaluated.

Many paint spray gun cleaning systems are currently in use throughout industry, each with individual emission characteristics. The challenge becomes selecting a system which cleans well, yet minimizes VOC emissions. A simple approach to emission reduction might be to make sure the system uses a low vapor pressure solvent and is closed during operation. However intuitive, this approach may not always yield the desired results.

This paper will discuss a comparative study of VOC emissions between two paint spray gun cleaning systems. One of the systems was defined as "closed" (i.e. had a cover which remained closed during operation); the other system was "open" (i.e. had no cover). A comparison was also made using cleaning solvents with different vapor pressures to determine solvent/cleaning system interaction regarding emissions.

BACKGROUND

This comparative study was sponsored by Safety-Kleen Corporation, Elgin, Illinois, and conducted by IIT Research Institute (IITRI), Chicago, Illinois, during June 1992. Safety-Kleen Corporation provides parts cleaning services with associated recycling to the automotive aftermarket industry. IITRI is a nationally recognized research and test institute which provides advanced research and testing to government and industry covering a diverse group of topics including environmental issues.

The comparative study was performed to demonstrate equivalent compliance with California South Coast Air Quality Management District (SCAQMD) Rule 1171, effective July 1, 1992. This rule requires that spray paint gun cleaners limit emissions of volatile organic compounds (VOC's) that are "stratospheric ozone depleting or global-warming compounds." The rule provides specific guidelines for the use and disposal of solvents used for spray paint gun cleaning systems (systems are defined as the cleaning unit and its solvent).

The principal aspects of the rule which deemed the study include:

- 1. The cleaning equipment must be "closed" during operation except when depositing and removing objects to be cleaned, and is closed during nonoperation with the exception of maintenance and repair to the cleaning equipment itself.²
- The solvent shall have a VOC content of "950 grams or less of VOC per liter of material and a VOC composite partial pressure of 35 mmHg or less at 20°C (68°F)."
- 3. Manufacturers, owners and operators may demonstrate equivalency (i.e. equivalent compliance) for a spray paint gun cleaning system in lieu of complying with these rules.⁴

Specifically, the Safety-Kleen Model 1107 Spray Paint Gun and Equipment Cleaner is considered by SCAQMD to be an open unit (i.e., does not have a cover); therefore, it does not comply with the specific provision of Rule 1171. Additionally, the solvent currently used with Model 1107 in California has a composite partial pressure of 96 mmHg, which exceeds the "35 mmHg or lower" requirement of Rule 1171.

However, the "equivalency provision" of Rule 1171 allows for a temporary exemption if it can be demonstrated that a "non-compliant" system does not lose more solvent than a currently accepted system.

This study performed by IITRI was designed to determine whether the Safety-Kleen Model 1107 had solvent losses comparable or less than hose of closed systems using a low (less than 35 mmHg) vapor pressure solvent. A Herkules GWR spray paint gun cleaner with a low vapor pressure solvent was selected for this comparative compliance study.

TEST PLAN

A Safety-Kleen Model 1107 and a Herkules Model GWR were tested for both active and passive solvent losses. Active solvent losses were those which occurred from cleaning a spray paint gun according to the manufacturer's recommended cleaning procedure for each system. Passive solvent losses were those which occurred as each unit would normally be stored between active cleaning cycles.

Solvent losses for active and passive tests were determined separately to permit total loss computation for any combination of active uses per day with the corresponding times between use.

Solvent losses were determined by precise weight difference measurements of each unit with its solvent. A highly sensitive precision platform scale was utilized for all weighing. The test procedures used standard weights to verify accuracy and sensitivity of the scale throughout the testing.

Active test weighing were made immediately prior to the start of an active test and at the completion of a cleaning cycle. The active cleaning cycle for each unit will be discussed in detail under "Active Test Procedures." Ten successive cleaning cycles comprised a single active test.

Passive test weighing were made daily for each unit. A single passive test lasted for five contiguous days at ambient laboratory conditions.

Environmental conditions in the laboratory were not controlled; however, temperatures, relative humidities and air velocities were periodically recorded during testing. Each series of tests were conducted virtually simultaneously in the same laboratory to minimize variations resulting from ambient environmental variations.

Two primary solvents were tested: Safety-Kleen $5820~{\rm West}^5$ (vapor pressure - 95 mmHg) and Grow 4231 P,N,C⁶ (vapor pressure - 32 mmHg). Both

solvents were cross-tested in both units to verify representativeness and to preclude test bias.

A third solvent, SK-East⁵, produced by Safety-Kleen, was also used for cross-testing. SK-East has a vapor pressure of approximately 75 mmHg.

A fourth solvent, cyclohexane (vapor pressure - 78 mmHg), was used in one series of active tests in the Safety-Kleen Model 1107 unit as a control solvent. Cyclohexane was used to establish active losses for possible future product developments. This solvent is available from a number of sources as a high-purity organic of known vapor pressure. Since this solvent is a single organic chemical with no isomers, it provides a valuable link between test results from this study and future experiments. It may also allow for future comparative losses from multicomponent solvents by simply comparing vapor pressures.

All testing was performed solely by IITRI staff at its principal laboratories in Chicago, Illinois. All units were operated in strict accordance with manufacturer's instruction manuals. 7,8 In addition, all active tests were conducted by a single operator to avoid inter-operator performance differences.

The active test plan consisted of three test series (A through C). (See Table 1 below.) Series "A" compared the Safety-Kleen and Herkules units using S-K East and Grow 4213 solvents, directly. Series "B" and "C" provide similar cross comparison, but also permit comparison within a manufacturer's unit.

TABLE 19
ACTIVE TEST MATRIX

Series	Test	Cleaner Unit	Cycles	Test Function	Solvent
A	1	Safety-Kleen(SK1)	10	Standard Clean	SK-East
A	1A	Safety-Kleen(SK1)	10	Repeat of Test 1	SK-East
A	2	Safety-Kleen(SK2)	10	Standard Clean	5820 West
A	3	Safety-Kleen(SK3)	10	Standard Clean	Grow
A	4	Herkules(H1)	10	Standard Clean	Grow
A	5	Herkules(2)	10	Standard Clean	SK-East
В	6	Safety-Kleen(SK1)	10	Replicate of Test 1	SK-East
В	7	Safety-Kleen(SK2)	10	Compare to Tests 3&4	Grow
В	8	Safety-Kleen(SK3)	10	Compare to Tests 2&11	5820 West
В	9	Herkules(H1)	10	Compare to Tests 5&15	SK-East
В	10	Herkules(H2)	10	Compare to Tests 4&14	Grow
С	11	Safety-Kleen(SK1)	10	Compare to Tests 2&8	5820 West
C	12	Safety-Kleen(SK2)	10	Compare to Tests 1&6	SK-East
С	13	Safety-Kleen(SK3)	10	Replicate of Test 3	Grow
С	14	Herkules(H1)	10	Replicate of Test 4	Grow
С	15	Herkules(H2)	10	Replicate of Test 5	SK-East
G	26	Safety-Kleen	10	Control	Cyclohexane

Note: Test lA repeated to correct procedural error.

The passive test plan consisted of two test series, "D" and "E" (See Table 2 below.)

TABLE 29
PASSIVE TEST MATRIX

Series	Test	Cleaner Unit	Days	Test Function	Solvent
D	16	Safety-Kleen(SK1)	5	Standard Passive	SK-East
D	17	Safety-Kleen(SK2)	5	Standard Passive	5820 West
D	18	Safety-Kleen(SK3)	5	Standard Passive	Grow
D	19	Herkules(H1)	5	Standard Passive	Grow
D	20	Herkules(H2)	5	Standard Passive	SK-East
E	21	Safety-Kleen(SK1)	5	Compare to Test 17	5820 West
E	22	Safety-Kleen(SK2)	5	Compare to Test 18	Grow
E	23	Safety-Kleen(SK3)	5	Compare to Test 16	SK-East
E	24	Herkules(H1)	5	Compare to Test 20	SK-East
E	25	Herkules(H2)	5	Compare to Test 19	Grow

TEST EQUIPMENT

Safety-Kleen Model 1107

Three identical new units, identified as SK-1, SK-2, and SK-3 were utilized in the study. The Safety-Kleen unit is an air-powered, dual-remote reservoir system consisting of a hemispherical cleaning/drain area with vapor collection collar and vacuum operated final rinse purge. The dual remote closed reservoirs, one for spent solvent and one for clean final rinse, provide for quick return of solvent to separate containers, minimizing potential for evaporation. The two air-driven solvent transfer pumps are centrifugal type to minimize solvent vapor evolution. Solvent vapors in the hemispherical cleaning drain area are removed through a perimeter collar venturi system and ducted where deemed appropriate by the user. This collar creates a slight negative pressure, keeping vapors contained and away from the user. In addition, the collar vapor collector is interlocked with the solvent pumps to preclude solvent pumping in the event of collar vapor collector malfunction. A vacuum canister is also provided to capture solvent during the final rinse purge stage. This canister is fitted with a coalescing media that gathers the solvent vapor, condenses it and returns it to the remote reservoir.

Herkules Model GWR

Two virtually identical, new units identified as H-1 and H-2 were utilized in the study. The Herkules unit is an air-powered, non-remote reservoir system consisting of a rectangular solvent storage tank with integral cleaning/drain area and a closable lid. The rectangular solvent storage tank is nominally filled with five gallons of solvent. The tank is also equipped with an external ball valve for draining during solvent change-

out. The unit is equipped with four equipment cleaning nozzles to accommodate the cleaning of two spray paint guns with paint cups simultaneously. The solvent transfer pump is a positive displacement type interlocked with the lid opening/closure.

Spray Paint Gun

Five identical, new paint spray guns were used for the study. One paint spray gun was dedicated to each cleaner unit. The paint spray gun was manufactured by Binks, Model 98-1130. This particular paint spray gun was selected because of its wide use throughout industry.

MEASURING EQUIPMENT

Platform Scale

A new, high precision Sartorius scale (Model F150) with a capacity of 150 Kg was utilized for all solvent weighing. The published scale sensitivity was one gram over the full range of 0 to 150 Kg. The scale was set up and calibrated by a factory-trained technician at IITRI prior to testing. The sensitivity was verified subsequent to set-up and calibration.

Sensitivity and accuracy tests at load were performed using Class S-1 weights traceable to the National Institute of Standards and Technology and six, 11.3 Kg barbell weights to provide loads slightly greater than the paint spray gun cleaner weights. Additional standard (Class F) calibration weights borrowed from the factory technician were used to produce loads over the full range of the scale.

Weights were added to the scale ranging from one gram to 150 Kg noting the values. A one-gram weight was added at each load to verify that the scale could detect the one gram. The scale responded precisely to the one-gram addition at all loads.

Scale Accuracy Verification

Throughout active and passive testing, the accuracy of the platform scale was verified prior to and immediately after each cleaning unit weight measurement. This was accomplished by placing the six 11.3 Kg weights in the marked "footprint" and recording the value. Then a 50 g weight was added and the value verified to become +50 g. Finally, all weights were removed; and the scale was checked for "zero tare."

Auxiliary Scale Platform

The original platform of the Sartorius scale was too small to accommodate the Safety-Kleen cleaning system. Therefore, a larger, aluminum, auxiliary platform was placed over the existing platform and remained for the duration of the testing.

The scale was sensitive to gross misplacement of the load, which may have led to erroneous readings. Therefore, prior to testing, the auxiliary platform was marked with the "footprint" of each cleaner and the barbell

weights. The loads throughout testing were placed in the marked location each time to preclude error.

ACTIVE TEST PROCEDURES

The following is a synopsis of the steps used to determine active solvent losses for each unit.

Safety-Kleen Model 1107

- 1. Weigh the cleaner and components. Record value and time.
- 2. Don gloves and safety goggles. Disassemble the unused, clean spray gun if it is not already apart, and place the parts in the cleaner bowl. Turn unit on.
- 3. Fill the paint cup from the used solvent port for 7 seconds by counting 7 beats starting when the solvent begins flowing into the cup. Do not start counting when the pump actuator switch is depressed, because there is a delay of several seconds before the solvent flows. There will be a solvent afterflow of several seconds when the foot actuator switches released.
- 4. Brush the spray gun cup for 30 seconds as follows: a) Brush the inside walls for eight seconds using a sweeping rotary motion; b) Continue brushing the inside walls using a vertical stroke while rotating the cup; c) Brush the lip and outer, upper collar using rotary strokes for 10 seconds. Keep track of time using the metronome beats.
- 5. Place the brush in the cleaner bowl and assemble the spray head to the paint cup.
- 6. Shake the assembled spray gun containing the solvent for 15 seconds using a pendulum motion.
- 7. Place the spray tip against the suction canister spout and squeeze the trigger while pushing the suction canister up.
- 8. Maintain suction for 7 seconds.
- 9. Disassembly the spray gun. Place the spray head in the bowl and pour the remaining solvent into the bowl.
- 10. Add clean solvent to the paint cup for 7 seconds.
- 11. Rotate the paint cup on its side 1 and 1/2 times slowly for approximately 10 seconds to wet the inside paint cup surface, simulating the entrainment of residual pigments/resins.
- 12. Pour the solvent into the bowl.
- 13. Place the paint cup into the bowl upside down to promote drainage.

- 14. Invert the spray head and place its tube against the clean solvent delivery tube of the cleaner. Squeeze the trigger while the solvent flows for 7 seconds.
- 15. Turn the spray head upright and flush clean solvent from the cleaner onto the spray tip for 3 seconds while rubbing the tip with a gloved finger.
- 16. Place the spray head into the bowl.
- 17. Remove and drape the gloves onto the bowl ledge and turn the unit off.
- 18. Disconnect the grounding clips and attach them to the cleaner so they are part of the system weight.
- 19. Remove the exhaust hose from the hood and place it so the hood end rests in the bowl.
- 20. Weigh the cleaner and components at exactly 4 minutes after the unit was turned off. (This 4-minute wait period is included to permit time for solvent evaporation from the bowl and components.) Record the time.
- 21. Repeat steps 1-20 nine additional times.
- 22. Record system operating pressure, room temperature, relative humidity and air speed on the data form during the tenth cycle.
- 23. Remove the cleaner and solvent cans after the tenth cycle of active cleaning. Record the tare weight.

Herkules Model GWR

- 1. Weigh the cleaner and components. Record value and time.
- 2. Don respirator, gloves and safety goggles. Disassemble the unused, clean spray gun, if it is not already apart.
- 3. Open the lid and invert the spray gun cup over the short nozzle.
- 4. Remove the trigger lock from the cleaner chamber and attach it so the trigger remains in an open position.
- 5. Place the tube of the spray head onto a cleaner nozzle and close the lid.
- 6. Turn the cleaner on for 60 seconds, timing the operation with a stopwatch.
- 7. Adjust the solvent pumping rate to 2 cycles/second by matching the pump beat to the metronome.
- 8. Turn off the cleaner and wait 5 seconds.

- 9. Open the lid and remove the trigger lock, returning it to the reservoir.
- 10. Shake excess solvent from the spray head into the reservoir. Hang the spray head on the metal rod at the front of the cleaner.
- 11. Shake excess solvent from paint cup into the unit.
- 12. Close the lid, placing the paint cup upright on top of the lid.
- 13. Remove gloves and place them on top of the lid, and immediately start timing a 4-minute wait period (to permit solvent evaporation from the components outside the reservoir).
- 14. Disconnect the air compressor supply.
- 15. Weigh the cleaner and components in-place after exactly 4 minutes using a stopwatch for time.
- 16. Repeat steps 1-15 nine more times.
- 17. Record system operating pressure, room temperature, relative humidity and air speed on the data form during the 4-minute wait period of the tenth cycle.
- 18. Remove the cleaner after the tenth cycle of active cleaning. Record the tare weight.
- 19. Repeat standard weighing to verify scale precision and accuracy. This completes a single active test consisting of ten data points for solvent loss per cycle.

PASSIVE TEST PROCEDURE

The following is a summary of the steps used to determine the passive solvent losses for each unit. This procedure was the same for both units and consisted of the following steps:

- 1. Connect "fresh" solvent cans to the Safety-Kleen unit. Add five gallons of test solvent to the Herkules unit.
- 2. Perform daily scale calibration verifications.
- 3. Weigh and record each cleaner. Record time of weighing.
- 4. Repeat measurements at approximately 24-hour intervals for five additional days.

RESULTS

Active

The comparative tests show that the "closed" Herkules Model GWR with Grow 4213 (33 mmHg vapor pressure solvent) lost an average of

18.2 g/cycle during active cleaning. The Safety-Kleen Model 1107 "open" unit with 5820 West solvent (95 mmHg vapor pressure) lost an average of 12.7 g/cycle during active cleaning. The Herkules unit with Grow solvent (32 mmHg vapor pressure) lost 1.4 times more solvent than the Safety-Kleen unit during active test. (See Table 3 below.)

T	39	
ACTIVE	LOSS	RESULTS

Test	Unit	Solvent	Date	Cycles	Total Loss, G	G-Loss/Cycle
2	SK-2	5820 West	6-4-92	10	127	12.7 +/-1.5
8	SK-3	5820 West	6-5-92	10	132	13.2 +/-2.1
11	SK-1	5820 West	6-7-92	10	123	12.3 +/-1.1
		Average of	Safety-Klee	n Units w	ith 5820 West	12.7
Test	Unit	Solvent	Date	Cycles	Total Loss,G	G-Loss/Cycle
4	H-1	Grow	6-4-92	10	202	20.2 +/-1.9
10	H-2	Grow	6-5-92	10	162	16.2 +/-0.9
14	H-1	Grow	6-7-92	10	182	18.2 +/-1.4
		A	of Bowley 1	an Cum IIni	lts with Grow	16.2

Passive

The tests showed that the Herkules unit lost an average of 1.82 g/hour during the passive (non-cleaning) mode. The Safety-Kleen unit lost an average of 0.32 g/hr during the passive test period. The Herkules unit lost 5.7 times more solvent than the Safety-Kleen unit during the passive period. (See Table 4 below.)

TABLE 49
PASSIVE LOSS RESULTS

Test	Unit	Solvent	Period	Total Wt Loss	Avg G-Loss/Hr
17	SK-2	5820 West	9-14 Jun 92	32	0.27
21	SK-1	5820 West	14-19 Jun 92	42	0.37
		Average of	Safety-Kleen Gur	Cleaner Units	0.32
19	H-1	Grow	9-14 June 92	189	1.57
25	H-2	Grow	14-19 June 92	238	2.07
		Average	of Herkules Gum	Cleaner Units	1.82

CONCLUSION

All of us recognize the importance of minimizing VOC and toxic air emissions in the coating industry -- not just in the application of coatings or surface preparation, but in cleanup operations as well. The methods for potential reductions are as diverse as the processes themselves. For this reason, simple rules and guidelines appear to be the most effective means of reducing emissions. However well intentioned, the desired result -- significant emission reduction -- may not always be achieved.

As evidenced by the aforementioned comparative study results, appropriate emissions reduction controls may already be in place, but misunderstood. Just like a good book -- a paint gun cleaner can't always be judged by its cover.

REFERENCES

- 1. South Coast Air Quality Management District (California), Rule 1171, "Solvent Cleaning Operations," adopted August 2, 1991.
- 2. Ibid, subparagraph (C)(2)(C), page 1171-8.
- 3. Ibid, subparagraph (C)(1)(C), page 1171-6.
- 4. Ibid, paragraph (c)(7), page 1171-10.
- 5. Safety-Kleen Material Safety Data Sheet No. 82343.
- 6. Grow 4213 Material Safety Data Sheet.
- 7. Safety-Kleen Model 1107 Instruction Manual.
- 8. Herkules Model GWR Instruction Manual.
- 9. Illinois Institute of Technology Research Institute (IITRI) "Final Report--Compliance Study of the Safety-Kleen Model 1107 Spray Paint Gun Cleaner," dated 6-29-92.

SESSION 11

APPLICATIONS 2

PAPERS PRESENTED:

"Priority Manufacturing and Environmental Issues at Military Industrial Facilities"

by

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"Low-VOC Dual-Cure Aerospace Topcoat"

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St. Paul. Minnesota

"UV Pollution Prevention Technology in Can Manufacturing"

by

Erik T. Donhowe

Coors Brewing Company

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"Pollution Prevention Opportunities in the Manufacture of Paint and Coatings"

by

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PRIORITY MANUFACTURING AND ENVIRONMENTAL ISSUES AT MILITARY INDUSTRIAL FACILITIES

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INTRODUCTION

Concurrent Technologies Corporation (CTC), a not-for-profit company, operates the Department of Defense's (DoD) National Defense Center for Environmental Excellence (NDCEE) which is located in Johnstown, PA. The NDCEE provides a means of testing, evaluating, and applying new and "state of the market" environmentally acceptable technologies in a low-risk industrial setting.

In 1990, Congress passed legislation that created the NDCEE. Sponsored by DoD's Office of the Deputy Assistant Secretary (Environment) and managed by the U. S. Army Material Command, the NDCEE was given the broad charter to systematically address industrial challenges and identify and implement environmentally acceptable solutions.

The broad scope of our mission gives us the flexibility to lead government and industry conversion to environmentally acceptable manufacturing technologies and to serve as a national resource for environment-related technical and analytical support. As the Center's infrastructure is put in place, it will gradually address:

- waste minimization.
- hazardous waste management,
- management of RCRA-type wastes,
- municipal-type solid waste and incineration issues,
- air pollution management,
- medical waste management,
- contaminated site remediation,
- demilitarization,
- recycling and recovery,
- water pollution management,
- nuclear waste management, and
- mixed waste management.

However, the initial thrust of the NDCEE will be that of Pollution Prevention --- specifically, demonstrating and exporting environmentally acceptable technologies to the DoD and defense-related industries.

HIGH PRIORITY ENVIRONMENTAL IMPACT REPORT

To ensure that the NDCEE focuses its attention on the nation's most significant manufacturing and environmental problems first, the NDCEE has prepared a High Priority Environmental Impact Report. For this report, industrial manufacturing technologies were analyzed and ranked according to their potential for adverse environmental impact and relevance to DoD- and defense-related industrial operations.

There is little information available that describes environmental discharges from DoD manufacturing facilities. Consequently, the NDCEE used the Toxic Release Inventory (TRI) industrial database, provided by the U. S. Environmental Protection Agency (EPA), for the analysis of potential adverse environmental impact. The TRI is the most comprehensive database available for industrial toxic air, water and solid waste discharges.

From the TRI listing of more than 300 chemical and chemical compounds, the NDCEE defined "high priority chemicals" as those which are:

- currently regulated by EPA,
- proposed to be regulated by EPA,
- identified as ozone depleting substances, or
- identified as potential, probable or known human carcinogens.

There were 68 chemicals in the TRI that met the criteria listed above. These chemicals represent 71.4 percent of the total TRI-reported discharges in 1989. Industries that discharge these "high priority chemicals" were classified according to three digit Standard Industrial Classification (SIC) codes and were ranked according to the total discharge of the chemicals. From the ranked listing of industries, those with operations similar or identical to manufacturing processes at DoD industrial facilities (e.g., electroplating) were selected as high priority.

The five selected SIC Codes with their total TRI discharge are: 347 - Coating, Engraving and Allied Products; 367 - Electronic Components and Accessories; 371 - Motor Vehicles and Motor Vehicle Equipment; 372 - Aircraft and Parts; and 373 - Ship and Boat Building and Repairing. The total TRI discharges and "high priority chemical" discharges from these industries are listed below. These industries will receive initial consideration by the NDCEE for environmentally acceptable replacement technology demonstrations.

SIC	TRI Total Discharge	"High Priority Chemical" Discharge
347	69.4 million pounds	52.2 million pounds
367	74.1 million pounds	57.5 million pounds
371	161.7 million pounds	151.4 million pounds
372	56.0 million pounds	50.6 million pounds
373	30.1 million pounds	29.7 million pounds

The NDCEE also conducted telephone interviews with companies in each of the five selected industries. Through these interviews, we were able to identify the top manufacturing-

related environmental issues, the associated manufacturing processes, technologies being considered to solve the environmental problems, and areas where the NDCEE could help.

CROSS INDUSTRY ISSUES

"High priority chemicals" discharges, which are common to three or more of the five selected industry segments, represent over 99.7 percent of the "high priority chemical" discharges. This indicates a high level of similarity in manufacturing operations among the five selected discrete parts manufacturing industries. Based upon the "high priority chemical" discharges of these industries, the following discrete parts manufacturing process activities can be inferred for the five selected industry segments:

- painting
- metal plating
- paint stripping
- metal cleaning

The sheer volume and breadth of the TRI discharge data gives the impression of fragmented and diffuse manufacturing-related environmental problems. The findings of this report suggest otherwise, since many industries face the same problems. In this High Priority Environmental Impact Report, the NDCEE has been able to distill these problems into the following seven cross-industry manufacturing related environmental needs for the five selected industries:

- demonstrate acceptable alternatives for paint removal chemicals,
- demonstrate acceptable alternatives for chlorinated and volatile organic compounds used as metal cleaners and paint solvents,
- demonstrate pollution prevention strategies and technologies to reduce heavy metal wastes,
- demonstrate acceptable alternatives to solvent based paint systems,
- implement a broader, more diligent effort for technology transitioning,
- provide worker training on pollution prevention practices and manufacturing technologies, and, finally,
- leverage scarce financial and human resources to solve common problems.

RECOMMENDATIONS

Based upon the NDCEE's findings, eight preliminary recommendations are offered. These recommendations are intended to stimulate discussion, upon reviewing this work effort, among members of the NDCEE's Senior Board of Advisors and Executive Advisory Council, as well as other interested individuals and organizations. Conclusions and further recommendations from those discussions will be incorporated into future considerations of the NDCEE.

The eight recommendations are specifically focused to action items for DoD and related industrial facilities which, if taken, would enhance the overall quality standard of these industrial facilities, as well as the overall environmental quality associated with the facilities and their products. The key features of these recommendations are:

- 1. Compile environmental discharge data from industrial facilities in a manner which relates those discharges to the processes used at the industrial facility.
- 2. Demonstrate alternative technologies which can resolve environmental discharge problems.
- 3. Conduct training programs on pollution prevention and alternative manufacturing technologies.
- 4. Link product and process specification requirements to environmental problems.
- 5. Implement standard for environmental costs; such as disposal and treatment, as well as "hidden" environmental costs; such as compliance, reporting, and monitoring.
- 6. Establish cost standards for "hidden" environmental costs; such as compliance, reporting, and monitoring.
- 7. Establish financial incentive programs to encourage pollution prevention practices.
- 8. Enhance the awareness of, and benefits from, pollution prevention alternatives through effective technology transitioning.

(The work described in this paper was not funded by the U.S. Environmental Protection Agency. The contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.)

LOW VOC DUAL-CURE AEROSPACE TOPCOAT1

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INTRODUCTION

The U.S. Environmental Protection Agency, as well as state and local regulatory agencies are in the process of implementing increasingly stringent controls on the emission of volatile organic compounds (VOCs). These emissions are the primary cause of photochemical smog and ozone pollution. Approximately seven billion pounds per year of VOCs are currently released to the atmosphere. A significant portion of this total is the result of industrial painting and coating operations. Mandated reductions in VOC emissions have led to the development of low or no VOC coating formulations by the coatings industry. Unfortunately, the reduced VOC content in these new formulations has often required a sacrifice in performance, appearance, or ease of application.

This paper describes development of the 3M dual-cure process for photocured high-performance coatings. Dual-cure involves the simultaneous polymerization of two monomer types to produce a material consisting of two independent but interpenetrating polymer networks (IPNs). The properties of these IPNs are often superior to either component separately. This novel cure technology may allow significant reductions in VOC content while maintaining the current performance characteristics of the cured coatings. Demonstration of the commercial feasibility of this technology is in progress in our laboratory with the support of the U.S. Department of Energy Office of Industrial Technologies under a cost-share contract. Performance testing is being done in collaboration with the Boeing Defense & Space Group. Aerospace topcoats have been selected for initial development efforts. These protective coatings have very high requirements for performance, appearance and durability. The materials currently in use are two-part polyurethanes which are spray applied. High resin viscosity requires the addition of a large

¹This paper was prepared for the U.S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, under DOE field office, Albuquerque, Contract No. DE-AC04-88ID12692.

amount of solvent to reach sprayable viscosity. The aerospace industry is under increasing regulatory pressure to find low-VOC alternatives for these coatings. To achieve substantial VOC reductions without a performance sacrifice has proven challenging. A dual-cure system consisting of a two-part polyurethane (polyol + isocyanate), combined with monomeric acrylates is being evaluated as a possible low-VOC replacement for urethane topcoats. The low viscosity acrylate component reduces the solvent required, while enhancing the performance of the cured film. Our goal is to produce a sprayable coating which meets the high-VOC performance specifications, but at a VOC content substantially lower than currently available alternatives.

California has established upper limits for VOC emissions by aerospace topcoats at 420 grams/liter (SCAQMD rule 1124). Previous to these regulations, high performance polyurethane topcoats typically had VOC levels of 650 grams/liter. It is likely that the regulations currently in force in California will eventually be adopted nationwide. To date, VOC compliant aerospace coatings have required some relaxation of the performance specifications established by the 650 g/l materials. Low-VOC coatings often have poorer appearance, are more difficult to apply and cure more slowly, and lack the chemical resistance of their high-VOC predecessors. Current low-VOC coatings are also at or near the maximum VOC levels allowed by current regulations. Traditional high-solids solventborne coatings technologies are unlikely to allow reduction much below current levels without an unacceptable decrease in performance.

DESCRIPTION OF THE 3M DUAL-CURE PROCESS

The basis of the 3M dual-cure process is a novel photocatalyst system which allows light activated curing of a variety of reactive monomers, including acrylates as well as polyols and isocyanates to give urethanes. The catalyst is an iron complex which can be decomposed to release catalytically active iron species upon exposure to visible or ultraviolet light. The photocatalyst structure and photodecomposition mechanism are illustrated in Figure 1.

Dual-cure catalysts are unique in their ability to photopolymerize polyols and isocyanates to produce polyurethane resins. Previously, all of the known polyurethane catalysts have been thermally activated. Light activation allows a degree of control of the polymerization process not possible using thermal catalysts. This characteristic can be utilized to provide a practical method for the preparation of IPN polymers.

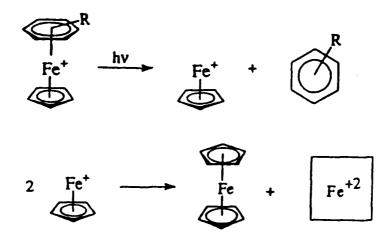
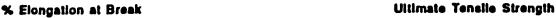
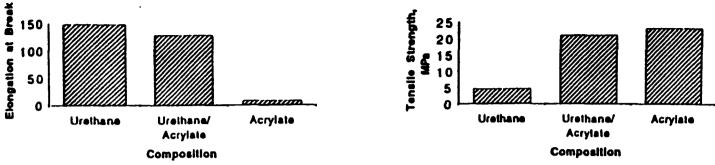


FIGURE 1. Chemical structure of the dual-cure photocatalyst and photodecomposition mechanism.

An interpenetrating polymer network is formed when two polymerization reactions, both which produce crosslinked networks, occur within the same space, but there is no chemical interaction between the two polymerization reactions. This produces two enmeshed polymer networks, both continuous throughout the entire solid, but with neither network connected to the other by any chemical bonds. For example, in the system chosen for aerospace applications, the two polymer systems are a polyurethane and a polyacrylate. The polyurethane is formed by an addition mechanism, while the polyacrylate is formed by a radical mechanism. The two polymerizations occur simultaneously, but independently of each other. The result is a solid composed of two interpenetrating networks, both continuous throughout the entire solid, but with no interconnections between the polyurethane and polyacrylate networks.

Materials having IPN morphologies often exhibit unusual mechanical properties. We have found in the polyurethane / polyacrylate IPN system that these materials exhibit the best properties of their constituent parts. For example, the tensile property data shown in Figure 2 is for an IPN composed of a strong but brittle polyacrylate, combined with a soft urethane with good elongation properties. The tensile properties of each component alone are shown for comparison. It can be seen that the tensile strength of the IPN approaches that of the pure acrylate, while at the same time maintaining most of the elongation of the pure urethane. The combined effect produces a material which is much tougher than either individual component. This is shown in the chart for energy to break, which is the integrated area under the stress / strain curve.





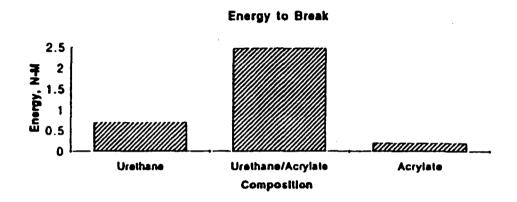


FIGURE 2. Tensile properties (elongation at break, strength at break, and energy at break) of a polyurethane / polyacrylate IPN material.

DEVELOPMENT OF DUAL-CURE AEROSPACE TOPCOATS

This enhancement of tensile properties led to consideration of polyurethane / polyacrylate IPNs for aerospace applications which have very demanding requirements for durability under a wide range of conditions. Several other criteria were established relating to requirements in the curing process. of the coatings must be activated with visible light exposure. Ultraviolet lamps were not an option because of the strong UV absorption exhibited by many common pigments. Fortunately, the dual-cure catalysts absorb weakly in the blue portion of the spectrum, which allows good cure of fairly thick pigmented films. Cure must also occur in air at ambient temperatures. inerting something as large as an airliner is not practical, and the number of potential users having heated hangers is limited. Normally, acrylate monomers do not cure well in air due to inhibition of radical cure by oxygen. In an IPN system, however, we have found that once the urethane cure has progressed sufficiently, oxygen permeability is reduced to the point that acrylate cure can occur. Cure has been demonstrated at

temperatures as low as 60°F, with no detrimental effects. As in conventional polyurethane coatings, complete cure is determined by the slow cure of the polyurethane, and development of final physical properties is obtained in approximately one week. Due to rapid acrylate cure, and the ability to use catalyst levels that would give unacceptably short potlife with conventional 2-part urethanes, very short tack-free times are possible. Current formulations require a 15 to 30 minute flash time for solvent evaporation, followed by a 10 to 15 minute light exposure, at which point the cured coatings are generally dry to touch.

A series of aerospace topcoat screening tests were selected with the assistance of Boeing personnel. These were taken from the Boeing commercial specification BMS 10-60, as well as military specification MIL-C-83286. Tests were chosen which were most critical to performance, and most difficult to meet simultaneously. These included VOC content, reverse impact, hydraulic fluid resistance (7 & 30 day), 60 degree gloss, low temperature flexibility, water resistance, salt spray corrosion resistance and pencil hardness. Accelerated weathering (500 hr. Xenon Weatherometer) was later added due to questions about the weatherability of non-urethane components.

This test series was used for the routine screening of experimental formulations. Formulations were tested over a VOC compliant water-reduced chromated primer (350 g/l VOC), on appropriately prepared aluminum substrates as detailed in the specifications. All initial screening was performed on samples containing titanium dioxide pigment at levels sufficient to achieve good hiding power. Cure has also been demonstrated with a variety of other colors. Reds appear to be the most difficult to cure due to competitive light absorption at catalyst absorption wavelengths, and cure speeds are slowed somewhat. Initial samples were knife coated and cured with 15 minutes light exposure. Testing was performed after allowing the samples to age for 7 days at room temperature.

The optimum formulation at this point consists primarily of polyurethane precursors, with a lesser amount of acrylate monomers. The acrylate present appears to improve low temperature and impact performance, as well as reducing the viscosity of the formulation. Current performance and specification requirements in the screening tests of several formulations are shown in the table on the following page.

·	Reference Specification	Criterion	Dual-Cure Performance
Pencil Hardness	BMS 10-60	<u>≥</u> 2B	Н
7 day Skydrol	MIL-C-83286	<pre>≤2 pencil loss</pre>	H(-0)
30 day Skydrol	BMS 10-60	<u>></u> 2B	HB(-2)
Reverse Impact	BMS 10-60	80 inlb.	45 inlb.
60° Gloss	BMS 10-60	≥90 %	89%
500 hr weathering	BMS 10-60	≥70%	77%
Pot-life	BMS 10-60	>4 hours	>4 hours
Dry-time	MIL-C-83286	<2 hours	<1 hour

During optimization of the dual-cure formulation, the most serious problems encountered were in achieving high initial gloss, and satisfactory weathering performance. Low initial gloss was found to result from incomplete acrylate cure at the surface of the coating due to inhibition by oxygen. Stained transmission electron micrographs of film cross-sections showed depleted acrylate to a depth of several microns. This resulted in post-cure film shrinkage, and surface roughening if pigment This problem was solved through the addition of cowas present. catalysts which improved surface cure of the acrylate. Weathering improvements were achieved through reformulation of the urethane components to more weatherable types, and the addition of U.V. absorbers and light stabilizers. This improved weathering performance at the expense of impact flexibility, which fell to below specified levels. We are currently investigating methods to improve coating flexibility without sacrificing other performance properties.

Estimated VOC levels for initial dual-cure topcoat formulations are in the 300 gram per liter range. We are in the process of optimizing solvent composition and flow control additives for spray application with high-volume, low-pressure (HVLP) spray equipment. Final formulations will be evaluated in a full set of qualification tests at a Boeing facility.

CONCLUSIONS

The dual-cure process shows promise for protective coating applications requiring high levels of performance. The IPN polymer structure which is formed can provide enhanced performance, often exhibiting the best properties of each component. VOC levels substantially below those obtainable with

conventional high-solids technologies appear possible. Performance levels are approaching those required for aerospace applications, and further optimization of formulations is in progress.

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UV Pollution Prevention Technology in Can Manufacturing

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INTRODUCTION

Conventional printing operations, including those in metal decorative printing, utilize solvent based, or solvent-containing, ink and varnishes. As a result, conventional printing technologies produce significant VOC (volatile organic compound) and HAP (hazardous air pollutant) emissions. One newer technology, ultraviolet (UV) light initiated curing of coatings, has the potential to provide significantly lower air emissions. The Coors Brewing Company Can Manufacturing Plant has been utilizing this technology in full scale aluminum can production since 1975. This report details the significant pollution prevention provided by this technology, and additional associated significant benefits in cost savings, energy conservation and practical operation.

HISTORY

The Coors Brewing Company developed the country's first aluminum beverage can, a two-piece aluminum can, in 1959, and was instrumental in the transfer of aluminum can production technology throughout the beverage can industry. The Coors Can Manufacturing Plant, located in Golden, Colorado, is the largest aluminum can manufacturing plant in the world, producing approximately 4 billion cans a year. The plant currently produces aluminum cans exclusively for the beer beverage market.

Coors Can Manufacturing worked in partnerships with several companies in developing the UV curing technology for decorating aluminum cans. The initial push to convert to UV operation was motivated by a desire to increase can printing speeds and to reduce energy consumption, in addition to a desire to lower air emissions. In 1974, Fusions Systems Corporation and Coors developed UV oven equipment which could rapidly cure UV inks. These UV ovens were installed in full scale can production in 1975. Coors has worked with several chemical companies over the years in developing practical UV inks and over varnishes. These chemical vendors have included Borden, General Printing Ink, Akzo and Martinez Ink Company. The Coors plant is currently the only plant in the country using the UV technology.

TECHNOLOGY

The UV curing technology is used to apply the decorative exterior label on aluminum beverage cans. The printing process is a "wet on wet" application, in which a clear protective over varnish is directly applied on top of colored inks prior to UV curing. The UV chemicals are approximately 100% solids in content, with essentially zero solvent contents.

In the can printing process (Figure 1), colored UV inks are applied to printing plates; one plate for each image color. A rubberized blanket wheel rotates, contacting the printing plates, picking up each color in sequence. The end result is a complete color image on the blanket wheel. Formed "silver bullet" aluminum cans are carried on mandrels, rotate over the blanket wheel, and are coated with the color image. The cans are then immediately carried over an over varnish wheel, where the clear protective over varnish is applied over the ink. The cans are then carried on chains to vacuum belts, where they are transported to the UV oven. The vacuum belt supports the cans in proper geometry for curing through the UV oven. The entire process is very rapid: printing speeds are approximately 1600 to 1800 cans per minute, and the UV oven cures the coatings in approximately 0.7 seconds.

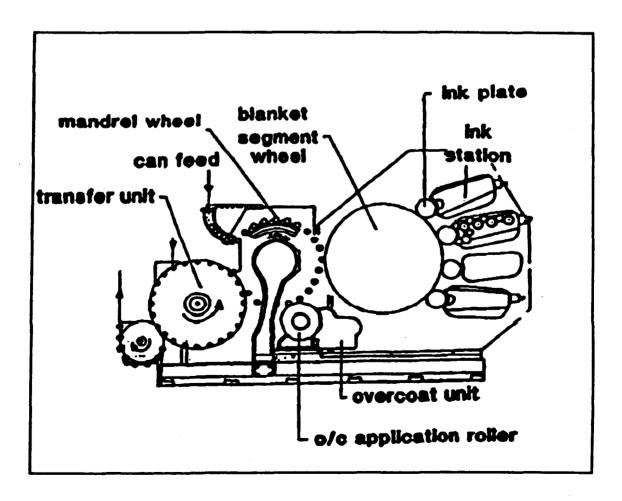


FIGURE 1. UV Can Printer

The alternative, conventional, technology used in other can manufacturing plants utilizes thermal curing of inks and over varnishes. The thermal curing ovens are natural gas fired, operating at 350 F or higher in order to achieve the ink and over varnish curing. Thermal ovens are approximately 60 to 80 feet long, 8 feet wide and 25 feet high. A long pin chain, approximately 400 feet long, is used the transport the cans through the oven. The large dimensions of the thermal oven, and the long transport chain, are required to provide the thermal contact time and still achieve production rates of 1500 cans per minute or higher (1).

The UV ovens, in comparison, are approximately 9 feet long, 5 feet wide and 5 feet high. The ovens operate at about 110 F, warmed slightly above ambient temperature due to the heat evolution from the UV lamps. Cans are transported to and through the oven on a vacuum belt. The UV oven contains between six and eight 10 inch, 300 watt/inch, microwave energized mercury lamps. The lamps are positioned with parabolic reflectors in a geometry to focus maximum illumination on the exterior surface of the aluminum cans. After an approximately 0.7 second exposure time, the cans leave the UV oven dry.

The print quality of the UV technology process is an important consideration. All cans produced at the Coors Can Manufacturing Plant are now made with the UV process, and print quality is comparable to that obtained with thermal curing. Similarly, color and gloss quality is equivalent to that obtained from the thermal process. The over varnish is applied in order to provide a protective coating over the decorative label; currently the abrasion resistance of the over varnish is dependent on the film thickness of the over varnish. For a fully commercial can market, with markets including all beverage categories in addition to the beer beverage, more technical development is needed to formulate a higher abrasion resistance. This should be achievable with newer formulations of UV over varnish (2).

The Coors Can Manufacturing Plant has in the past utilized a thermal technology can line side by side with the main UV technology can lines. As a result, production operators have had the opportunity to evaluate practical operations of the UV technology in comparison to the conventional technology. The UV ovens can be started up much faster that thermal ovens (only a 5 minute start up time is required). The controls for the UV ovens are simpler. The newer UV ovens utilize vacuum can conveyance belts, which are simpler, more reliable, and easier to maintain than the long 400 foot pin chains which transport cans through hot thermal ovens. The low operating temperature of the UV oven is also beneficial for front line production operation and maintenance. Maintenance and parts costs for UV technology have been estimated to be significantly lower than requirements for thermal technology (Table 1).

TABLE 1. OPERATIONAL EFFICIENCY

Oven Size	10% of Thermal
Downtime	Significantly Less
Maintenance	22% of Thermal
Parts	28% of Thermal
Process Control	Simpler
Energy Use	55% of Thermal

In conjunction with the higher operational efficiency of the UV process, there are associated financial savings. An estimated cost analysis has been performed for chemical usage, power consumption, natural gas usage and equipment maintenance costs (Table 2). Chemical costs are currently approximately 5% higher for UV inks and over varnishes. Natural gas is not required for UV ovens, therefore the UV technology provides an estimated savings of \$50,000 per billion cans produced. As previously mentioned, thermal ovens require more maintenance. Therefore, an estimated \$90,000 per billion cans savings is provided with UV technology.

TABLE 2. OPERATING COSTS (\$1000/BILLION CANS)

	<u>UV</u>	THERMAL
CHEMICALS	1,076	1,025
ELECTRICAL	60	57
NATURAL GAS	0	50
MAINTENANCE	40	130

The total energy consumption requirements have been compared for the UV and thermal technologies (Table 3). Estimates in units of millions of BTUs per billion cans are provided. The estimates include both BTU values obtained directly from natural gas (thermal ovens) and BTU values for the electrical power consumption. Since no natural gas is used with UV ovens, approximately 15,400 million BTUs are saved per billion cans. Both types of ovens require similar levels of electrical power. Electrical power consumption is slightly higher for UV than for thermal, due to the energy demands of the UV lamps, however the thermal ovens also require comparable electrical power to run blowers and can chain conveyors. The net energy savings with UV technology is estimated to be 14,880 million BTUs per billion cans produced.

TABLE 3. ENERGY SAVINGS (MMBTU/BILLION CANS)

	UV OVEN	THERMAL OVEN	ENERGY REDUCTION
NATURAL GAS	0	15,400	15,400
ELECTRICAL	10,500	9,980	-520
		TOTAL	14,880

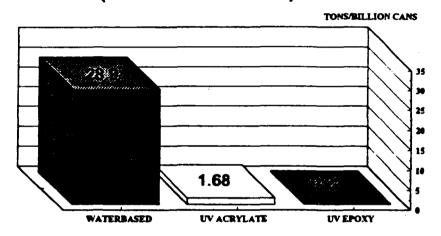
ENVIRONMENTAL IMPACT

Over the past two years, a series of procedures have been conducted at the Can Manufacturing Plant to estimate the environmental impact of the UV printing technology. The procedures ranged from the laboratory analysis of ink and over varnish VOC contents to full EPA protocol stack testing. This analysis has provided a comparison of the UV to the thermal conventional technology.

An initial estimate was made utilizing ASTM method 24 testing of the thermal and UV inks and over varnishes. Method 24 is the approved method for determining VOC content in paints

and other surface coatings. The method was modified to add UV curing prior to the gravimetric analysis in the procedure, in order to accurately reflect the UV initiated cross-linking of the inks and overcoats. Results were expressed in tons of VOCs per billion cans. The data (Table 4) indicates that the current generation of UV coating, UV acrylate, contains 1.68 tons of VOC per billion cans, which is substantially lower in VOC content that the current water based thermal coating, which contains 28.9 tons per billion cans. A newer UV coating product with potential production application contains an even lower VOC content of 0.22 tons per billion cans.

TABLE 4. COATING VOC CONTENT (MODIFIED METHOD 24)



An initial estimate of actual stack emissions was conducted on the UV oven exhaust from a can line running at full production rates. The method used was EPA Method 18, a general method allowing the use of various procedures for sampling and instrumental analysis. The conditions chosen were charcoal tube absorption followed by solvent desorption and GC/MS analysis. Based on the UV chemical formulations, specific target compounds were selected. The results of this screening test (Table 5) indicated that target compounds were not detectable to the detection limits of 1 ppb (w/v). Corresponding emission calculations in tons/year of VOCs indicated that emissions were less than 0.3 tons/year for each target, and a total less that 1.5 tons/year.

TABLE 5. VOC EMISSIONS ESTIMATE
(EPA METHOD 18 SCREEN)

COMPOUND	ug/L	TONS/YR
n-butanoi	< 5	< 0.3
ethoxyethanol	< 5	< 0.3
o-xylene	< 5	< 0.3
ethoxyethoxyethanol	< 5	< 0.3
benzophenone	< 5	< 0.3
	TOTAL =	< 1.5

Additional estimates of VOC emissions were obtained from Material Safety Data Sheet (MSDS) data for the VOC content of each coating product (Table 6). Comparisons were made for the over varnish (overcoat), ink and bottom varnish (bottom coat) applications. The application of a varnish on the bottom of the cans was estimated for the UV process as a conservative comparison, even though bottom coat is not applied currently in the UV process. Very significant differences are evident between the thermal and UV processes with this estimate. The VOC emissions are again based on a tons/billion cans basis, as this is the index generally used for regulatory control. A total of 28.5 tons of VOCs are estimated to be released as VOCs with the thermal process in comparison to a conservative maximum emission of 1.6 tons/billion cans for the UV process.

A similar comparison (Table 7) was made for hazardous air pollutants (HAPs). Almost half of the VOC content in current thermal coatings are glycol ethers, which are listed hazardous air pollutants in the new Clean Air Act regulations. It is pertinent, therefore, that, with upcoming higher scrutiny and tighter controls for HAPs, a technology with lower HAP emissions will be highly preferred. Estimated HAP emissions from the thermal technology are 14.3 tons/billion cans, and estimates from MSDS data indicate that there are no HAP emissions at all for the UV technology.

TABLE 6. ESTIMATED VOC EMISSIONS

(MSDS DATA - TONS/BILLION CANS)

	THERMAL	<u>UV</u>
OVERCOAT	26.5	1.3
INK	0.8	0.2
воттом соат	1.3	0.1
TOTAL	28.5	1.6

TABLE 7. ESTIMATED HAP EMISSIONS

(MSDS DATA - TONS/BILLION CANS)

	THERMAL	<u> UV</u>
OVERCOAT	13.2	0.0
INK	0.4	0.0
BOTTOM COAT	0.7	0.0
TOTAL	14.3	0.0

Proposed HAP regulations at the federal regulatory level, and current HAP regulations at the state regulatory level, require emissions reporting at very low reporting thresholds. Current OSHA standards stipulate MSDS reporting thresholds for chemicals at 1% and 0.1% concentrations. This data was judged to be too inaccurate for appropriate HAP regulatory reporting needs. Therefore, protocol testing was conducted on the UV process at the Coors Can Manufacturing Plant. This detailed stack testing was conducted in order to fully comply with our current state HAP reporting thresholds at 50 and 100 pound/year levels. The data from the protocol stack testing (Table 8) indicated that extremely small levels of HAPs are emitted. The compounds detected were suspected to be present in the UV chemicals as trace constituents. It is important to note that only 360 pounds are emitted for the entire facility per year. The UV technology is therefore essentially a zero HAP process.

TABLE 8. HAP EMISSIONS (PROTOCOL TESTING)

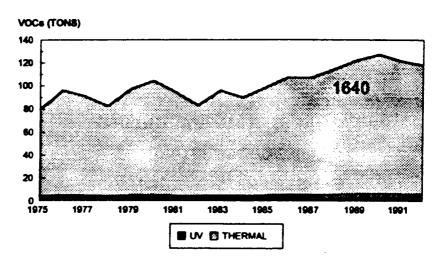
HAPS	LB/YR ·
MEK	67.3
XYLENES	42.9
METHANOL	72.1
TOLUENE	124.7
FORMALDEHYDE	53.4
TOTAL	360.4

Entire Facility

The Coors Can Manufacturing Plant implemented the UV printing technology in 1975, and the plant is the only can manufacturing plant using this technology. If the conversion had not taken place in 1975, significant emissions of VOCs and HAPs would have occurred. The implementation of the UV operation has thus had a very significant pollution prevention effect. The magnitude of this is depicted in Figure 1. The upper part of the chart is the potential emissions from a thermal process; the small lower area of the chart depicts the worst case estimate for UV technology emissions.

Approximately 80 to 100 tons of VOCs would have been emitted each year since 1975. The sum of these savings in potential emissions is 1,640 tons of VOCs. This comparison is conservative, since it is based on VOC contents of current UV and current thermal coatings, and earlier thermal coatings were much higher in solvent content.





In addition to VOC and HAP emissions, CO₂ emission estimates were compared for the two technologies. The CO₂ estimates are calculated from EPA conversion factors for natural gas combustion, and also for CO₂ emission factors for electrical power production. The CO₂ estimates for the UV technology therefore include the CO₂ emissions which occur at the power plant generating the electrical power used for the UV process. The annual emissions savings at the Coors Can Manufacturing Plant due to the UV technology are currently estimated to be 107.6 tons of VOCs, 57.0 tons of HAPs, and 4,216 tons of CO₂.

If the UV technology were transferred nationally, there would be subsequent notable pollution prevention impacts. Estimates for a national technology impact have been calculated by comparing the annual production of approximately 4 billion cans/year at the Coors Can Manufacturing Plant to the national production rate. The national production of aluminum beverage cans is approximately 100 billion cans/year (3).

Pollution prevention estimates (Table 10) are 2,690 tons/year of VOCs, 1,425 tons/year of HAPs, and 105,400 tons/year of CO₂ emissions. These impacts are even more substantial taking into account the regional clustering of can manufacturing plants in several states. The

implementation of UV technology could therefore have a significant regional pollution prevention impact.

TABLE 9. EMISSIONS SUMMARY

ENTIRE FACILITY - TONS/YR

	ACTUAL (UV)	THERMAL	ANNUAL REDUCTIONS
voc	6.4	114.0	107.6
HAP	0.2	57.2	57.0
CO2	4200	8416	4216
<u> </u>			

TABLE 10. EMISSIONS SUMMARY

NATIONAL POTENTIAL - TONS/YR

	ACTUAL (UV)	THERMAL	ANNUAL REDUCTIONS
voc	160	2850	2690
HAP	5	1430	1425
CO2	105,000	210,000	105,400

SUMMARY

The UV curing technology in use at the Coors Can Manufacturing Plant has been a proven technology for the past 18 years. Very substantial benefits are evident with this technology in very low, or zero, VOC and HAP emissions, and much lower CO₂ emissions as compared to the alternative thermal curing technology. Estimates also indicate that the UV technology consumes less energy than the thermal technology, and that the UV technology is operationally more cost effective than the alternative technology. The UV technology at the Coors plant is currently dedicated to a beer beverage market, and can product quality is fully acceptable for this market. A higher abrasion resistance can coating is currently desired for other beverage markets. Therefore newer generation UV over varnishes with higher abrasion resistance ratings may have to be investigated or implemented in order to fully convert this technology. In light of the significant pollution prevention effects from this technology, and more stringent upcoming air regulations, it would seem to be desirable to overcome these remaining minor obstacles.

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POLLUTION PREVENTION OPPORTUNITIES IN THE MANUFACTURE OF PAINT AND COATINGS

BY

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Abstract

The paints and coatings industry is rapidly changing to meet environmental and economic pressures. Some of the changes include new coating formulations, higher performance finishes with improved properties, continued development of new technologies, and new application methods with improved transfer efficiencies. In order to control costs, improve productivity and quality, and protect the environment, more paint companies are turning to pollution prevention as the cornerstone of their waste management programs. Paint pollution prevention has been incorporated into many corporate total quality management (TQM) strategies.

There are many pollution prevention methods for the paint manufacturing industry which vary from very simple, inexpensive measures to new, expensive plant/equipment. The methods, techniques or programs can generally be classified as either recycling or source reduction and may involve material substitution, process or equipment modification, revised operating practices, operating procedures (such as waste stream segregation), personnel practices (such as operator training), loss prevention practices, or accounting practices. This paper will provide an overview of these practices in-place at particular manufacturing facilities to reduce wastes and associated costs, to be a more competitive industry that must still maintain quality and performance of its products.

The information in this article has not been subjected to Agency review. Therefore, it does not necessarily reflect the views of the Agency.

Introduction

The role of the paint and coatings industry in the U.S. economy is pervasive. Paint and coatings are essential not only for the decoration and protection of the surfaces of many new industrial products but also for the maintenance of existing structures and products, such as homes, vehicles, machinery and equipment, buildings and factories. Without these paint and coatings, many of our durable and non-durable goods would have a decreased life-span.

The manufacture of paints and coatings is big business with shipments exceeding \$11.5 billion (1989) in the U.S. alone. Americans consume approximately 1 billion gallons annually, of which, approximately 50 percent is represented by architectural coatings. The annual growth rate for the industry is expected to be 1 percent (1991-1996). The product coatings area accounts for about 36% of (1991) shipments and special purpose coatings with 16% of 1991 shipments. The nine industries that are major consumers of paint and coatings include: (1) automotive; (2) trucks/buses; (3) metal cans; (4) farm machinery/equipment; (5) construction machinery; (6) coil coating; (7) wood furniture/fixtures; (8) metal furniture/fixtures and; (9) household appliances.

The driving forces behind the changes in paints and coatings continue to be product performance improvements and environmental regulations associated with new materials.

Paint and coating formulators as well as upstream raw material and resin suppliers are evaluating the components in their products and processes, changing the constituents to achieve desired performance of their coatings while also meeting new environmental rules. Paint producers undertake their own product research and development but also look to technological leaders to meet reformulation needs.

In addition to addressing product reformulation impacts, paint and coatings manufacturers are also examining their production methods to look for ways to control costs. To achieve improved productivity and quality, as well as protect the environment, more paint companies are turning to pollution prevention as the cornerstone of their waste management programs. Pollution prevention methods generally involve material substitution, process or equipment modification, modified operating practices and procedures (such as waste stream segregation), personnel practices (such as operator training), loss prevention practices or accounting practices. This paper will provide an overview of the paint industry's efforts to reduce wastes and reduce costs, while at the same time provide quality paint and coatings products which meet the performance requirements of a diverse customer base.

Review of Raw Materials

The primary raw materials used by the paint and coatings industry include resins, pigments, solvents and additives. In the production of liquid paints (latex and solvent-based), production methods are primarily physical, that is, there are no chemical reactions or conversions of raw materials to other products and byproducts. Paint is typically a dispersion of a finely divided pigment in a liquid composed of a resin or binder and a liquid vehicle.

There is a wide variety of synthetic resins used in coatings (i.e. acrylic, alkyd, vinyl, epoxy, polyester, urethane, etc). The synthetic resins are long chain polymers that may be linear, branched, or cross-linked or some combination of these forms depending on the functionality and reactivity of the monomers from thick they are formed. Resins are selected based on many factors but primarily on application and performance.

The liquid portion varies depending on whether the paint is solvent based or water-based. Typical organic solvents include methyl ethyl ketone, methyl isobutyl ketone, toluene, and xylene. Water based, water dispersed, or water soluble coating systems substitute water for some or all of the volatile organic solvent.

Manufacturing Process Wastes

In the manufacture of paint and coatings, paint manufacturing facilities generate different waste streams. Typical wastes include:

- Raw material packages, bags, containers from unloading materials into mixing vessels.
- Pigment dusts from unloading of pigments into mixing vessels

- Solvent emissions from storage tanks, leaks, and open process equipment
- Off-spec paints
- Spills
- Rinsewater from equipment cleaning using water or caustic solutions
- Paint sludge from equipment cleaning operations
- Filter cartridges with undispersed pigment, paint and/or resins.

Paint industries handle this waste by either on-site recycling, off-site recycling or treatment/disposal. On-site recycling involves the selected reuse of raw materials or wash materials in new batches of paints and coatings. Recycling of usable materials within the plant reduces the amount of new virgin raw materials needed per batch, resulting in significant reductions in operating aw well as waste management costs. On-site recycling of solvents may include distillations. Many companies send their wastes to an off-site recycler, though more and more of these companies are recycling their own wastes to reduce costs and improve operating efficiencies. Treatment/disposal operations available to paint manufacturers include incineration or land disposal. Typically, many paint manufacturers send solvent-containing wastes off-site to a cement kiln for inclusion in a fuels-blending program (for thermal destruction).

Of the wastes generated in a typical paint manufacturing facility, equipment cleaning wastes are by far the largest in volume, collectively accounting for some 80% of the industry's wastes. Process equipment and tanks are routinely cleaned to prevent product contamination and/or restore operation efficiency. Equipment that may need cleaning include high speed dispersion mixers, sand mills, colloid mills, rotary batch mixers and blenders, drum mixers and roller, grinding equipment, mixing vessels, pumps & motors, filters and strainers, filling and capping equipment and packaging equipment. Many paint manufacturers are finding pollution prevention provides significant opportunities for reducing wastes.

Pollution Prevention Methods for the Paint Manufacturing Industry

Pollution prevention, or the method of preventing polluting through source reduction and recycling, is becoming a cornerstone of most progressive waste management programs. Reducing wastes to remain competitive has been an important ingredient for successful business in the past and it will be absolutely essential in the future. So controlling and optimizing all parts of the manufacturing process is critical to reduce costs, improve processes and continue to be competitive and profitable.

Pollution prevention approaches can be broken down into the following categories:

- Source reduction Good manufacturing practices, production process changes, and input material changes.
- Recycling use and reuse of wastes, reclamation (on-site, off-site recovery).

Good manufacturing practices generally means better procedural or institutional policies and practices and can include waste segregation, personnel/employee practices, procedural measures, loss prevention practices, and accounting practices. Personnel practices can include upper management initiatives, employee training, and/or employee incentives. Careful attention to production and maintenance operations is important to reduce spills and minimize off-spec products. Making employees more aware of the impact of waste on the company's costs as well as the impact on the environment.

Procedural measures can include better documentation, better material and handling storage, material tracking and inventory control and better production scheduling techniques. For example, since thousands of different paint formulations require special production runs, more effective planning and production scheduling may be needed. Paint production, although a vital phase, must intermesh smoothly with purchasing, formulation sales, accounting, inventory, personnel management etc. to make it profitable. Production planning and scheduling may consist of a scheduling board listing the batches to be run on each piece of equipment and the expected starting and finishing times. It aids maintaining adequate inventory of active raw materials without overstocking and permits attainment of delivery of commitments to customers. Also, if practiced effectively, it helps level peaks and slumps in production during surges of short delivery orders or establish "downtime" of each piece of equipment while keeping check of overall efficiency and ensuring maximum equipment utilization.

In loss prevention practices, better awareness of spill prevention and in house preventive maintenance programs may be required. Accounting practices should incorporated better apportionment of waste management costs to the departments that generate wastes.

Most off-spec paint is generated by small shops that produce specialty paints. Since the production costs for specialty paints are typically high, most off-spec paints are reworked into marketable products. However, the cost of reworking off-spec paints are avoided if better trained and supervised operators as well as quality control are reinforced so that generation of off-spec paints are avoided.

Obsolete paint products and customer returns can be blended into new batches of paint. Obsolete products result from changes in customer demands, new superior products, and expired shelf life. Careful production planning and inventory control can reduce obsolescence resulting from expired shelf life. Also marketing policies such as discounting older paints can help reduce the amount of obsolete products.

There are many other ways of applying good manufacturing and operating practices.

For example, soliciting employee suggestions may uncover methods to make changes especially since the operators understand the process operations. Quality improvement teams make significant improvements to the quality of the product, optimize the process, improve efficiency and productivity, and reduce the wastes in the process. Furthermore, incentives, rewards, and bonuses can be used to support pollution prevention programs and reduce wastes.

Improving the efficiency of a process can significantly reduce waste generation. Available techniques range from eliminating leaks from process equipment to installing state of the art production equipment. This pollution prevention category includes improved operation and maintenance, procedural changes, and equipment modifications.

Equipment cleaning wastes represents the largest source of waste in a typical paint plant. A method that reduces the need or frequency of tank cleaning or allow for reuse of the cleaning solutions is the most effective way to reduce wastes.

The use of mechanical techniques, such as rubber wipers, reduces the amount of paint left on the tank walls of a mix tank. Wipers are used to scrape the sides of a cylindrical mix tank (flat or conical). Equipment cleaning is usually a manual operation so this process may be justified based on rescued labor costs as well as reduced usage of cleaning solution (another savings). High pressure spray heads and limiting wash/rinse time systems can be used in place of regular hoses to clean water-based paint tanks. Studies show that high pressure wash systems can reduce water use by as much as 80 to 90 percent.

Teflon line tanks are sometimes used to reduce wall adhesion and improve drainage. This method is usually applicable to small batch tanks. A plastic or foam "pig" is used to clean pipes. This pig device is forced through the pipe from the mixing tanks to the filling locations, using nitrogen or some other inert gas to propel the pig.

Manufacturing procedures may be improved. For example, a paint facility's wash solvent from each solvent-based paint batch may-be separately collected and stored. When the same type of paint is to be made, waste solvent from the previous batch is recycled and used in place of virgin solvent.

Countercurrent rinsing processes can be applied to those plants with sufficient tanks space. This technique is used to recycle "dirty" solution initially to clean tanks and then is followed by a "clean" solution to complete the rinse cycle. The level of contamination builds up more slowly with the clean solution than the dirty reused solution thus extending cleaning solution life.

Spills due to accidental or inadvertent discharges usually occur during transfer operations or as a result of equipment failure. For example, during a loading operation, a spill may occur from a leaking fill hose or fill line connection or leaking valves, piping, and pumps. Sometimes spills occur from overfilling of tanks or due to improper or

malfunctioning overflow alarms. Improving regular equipment inspections and training programs prevent these spills from occurring as well as improved instrumentation and automation and efficient cleanup methods if spills do occur.

Small amount of dry materials used in paint may remain in bags. Capturing the pigments for reuse through vapor traps helps reduce waste problems. The availability of these materials in slurry or paste form eliminate problems of disposing of waste bags or packages. Empty containers of liquid raw materials that contain hazardous compounds are typically cleaned or recycled back to the original raw materials manufacturers or to a local drum recycler. This avoids the costs of disposing of the containers.

There are two major types of air emissions in paint manufacturing plants: VOCs and particulates. VOCs may be emitted from the conservation vents on top of the bulk storage tanks of resins and solvents and from the use of open processing equipment such as mix tanks. Since most process equipment is of open design, reducing VOCs from equipment could require substantial capital expenditure in retrofit costs. Closed vessels with overhead refrigerated condensers will require considerable capital requirements which most paint manufacturers cannot afford. In fixed roof design, maintained conservation vents, conversion to floating roof, use of nitrogen blanketing to suppress emissions or the use of refrigerated condensers. Implementing these options can result in cost savings to the paint and reduced raw material losses.

Dusts generated during handling, grinding, and mixing of pigments may be hazardous and therefore dust collection equipment such as hoods, exhaust fans, and bag houses are used. Use of pigments in paste form instead of dry will reduce or eliminate dust generated from pigments. The drums can be recycled.

Also, a major advance in paint manufacturing is the growing use of electronic control devices and batch automation. The intent is to avoid operational accidents, improve quality, and production efficiency, and the overall accuracy of the batch. The effect should be less waste generated. Computer use is increasingly being used for materials allocation and inventory control as well as preventive maintenance scheduling. As the costs associated with plant automation equipment decreases, the use of automation in paint manufacturing facilities will increase.

Case Studies

Four companies that have received special recognition for their pollution prevention programs by industry are Moline Paint Manufacturing co. in Moline, IL, Vanex Color, Inc. in Mt. Vernon, IL, Red Spot Paint & Varnish Co. in Evansville, IN, and Jamestown Paint Company in Jamestown, PA. Moline reported a 50% reduction of hazardous wastes in less than five years and reported savings of over \$140,000/yr in disposal and raw materials costs. Moline's program included on site recovery for reuse, process modifications, statistical process control techniques of waste generation, improved housekeeping, employee

participation, and reuse of hazardous wastes off-site in a waste-to-energy recovery program.

Vanex Co. used source reduction and recycling methods. Ethylene glycol, a free-thaw stabilizer in latex paints, has been replaced with propylene glycol which exhibits less health concerns. Wash solvents generated from the production of solvent-based paints is recycled, when possible, into subsequent solvent-based paint batches. Unusable wash solvent was sent to a cement kiln. Approximately 80% of all wash solvent was recycled in-house resulting in savings of \$15,000/yr.

Red Spot Paint & Varnish Co. initiated a full waste-tracking system to identify the exact point of origin of each unit process waste, which was then sampled and analyzed to determine its potential for recycling and reuse. The program concentrated on motivating employees to become more waste conscious and to train them in waste reduction methods and procedures. Through their program, the company saved more than \$1 million by incorporating a number of seemingly insignificant equipment additions and a few equipment and tool modifications, which represented over 60% savings.

Jamestown Paint Company incorporated pollution prevention into their total quality management (TQM) program by focusing on waste minimization, quality control, customer satisfaction and increased profitability. Employees drawn from various operational and administrative areas formed process improvement teams, and each team was given specific objectives and charged with clearly defined improvement goals. Results a year after implementation of the program showed a reduction in hazardous waste by more than 75% and savings in excess of \$100,000.

Pollution Prevention Techniques Applicable to Paint Manufacturing

The following summarizes some of the pollution prevention techniques paint manufacturers are using:

Source Reduction

- Schedule compatible solvents in sequence to reduce truck loading and drum flushing need.
- Schedule like colors through equipment.
- Install dedicated lines where feasible to reduce flushing.
- Segregate line and pump flushings to produce low-grade thinners suitable for cleaning purposes.
- Equip bulk storage tanks with vapor return lines.

- Install collector to remove pigment dust from manufacturing area.
- Increase drum inventories of high volume products to reduce changing of products in the drumming line.
- Replace wastewater treatment lagoons with new system incorporating concrete cells covered by fiberglass dome, equipped with venting of off-gases to destruction by burning.
- Eliminate dry bags by converting to titanium dioxide slurry system pumped directly to mixer.
- Install closed filtration systems to reduce VOC emissions (losses); also closed filter systems can eliminate residues once left in filter bags.
- Install odor/vapor capture systems on bulk solvent storage tanks, resin tanks and manufacturing tanks.
- Eliminate all obsolete materials for possible rework.

Reuse/Recycling in manufacturing process

- Recycle wash solvent whenever possible; to facilitate recycling, setup holding tanks for recovered washwater and wash solvent, segregate by color and/or product line; reuse wash solvents from one batch in the grind state of the next batch of the same formula.
- Collect pigment dust and recycle into batches.
- Reuse in batch production solvents used for cleaning sand mills, manufacturing tanks, and tankwagons.
- Reuse obsolete materials in present production.
- Use virgin solvent for tankwagon cleaning and reuse in subsequent production.
- Pass vapors generated during filling and manufacturing through filters to remove as much VOCs as possible; collect solvent that would otherwise have gone to atmosphere and use as wash solvent.
- Where possible, mix obsolete colors and sell as undercoat or primer.
- o Accumulate all skids not usable at plant and give to skid vendor.

- Recycle used motor oil from company vehicles.
- Reuse cardboard shipping cartons and plastic pails; return corner boards on can shipments to supplier.
- O Unrecyclable wash solvents can be used as supplemental fuel in cement kilns for energy recovery; establish contracts with cement kilns for recycling of unusable wastes with high BTU value.
- Inspect, repair, and reuse shipping pallets received with the purchase of raw materials or return to vendor.
- Rinse and crush metal containers and ship to scrap metal recycler.
- Recondition and recycle drums and five-gallon pails for use.

Conclusions

The paints and coatings industry will continue to seek new technologies to meet the growing needs and demands of our society. While there has been significant progress in the industry to reduce or eliminate waste, manufacturers of all coatings recognize that new environmental regulations may seek to significantly reduce their wastes even further. As a result, paint manufacturers will increasingly turn to pollution prevention techniques and methods to eliminate waste generation. Already, pollution prevention methods are making significant contributions to reduce paint wastes/sludges through source reduction, process/production techniques, good manufacturing practices, and material substitutions. The coatings industry's efforts will be important towards improving environmental quality. Many of the pollution prevention techniques developed by the paint industry are relatively simple and inexpensive and may only require a conscious change in operating procedures. Some changes such as new plant/equipment require greater monetary expenditures up front, but in the long run, may provide the company with significant cost savings and improved environmental quality.

Conclusions in this article are those of the author. No official support for these conclusions by the U.S. EPA is intended or should be inferred.

For Further information

There are many pollution prevention methods which have been published in various literature or can be obtained through industry contacts. For further information, please contact:

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APPENDIX A

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16. ABSTRACT The report documents a conference that provided a forum for the exchange of technical information on coating technologies. It focused on improved and emerging technologies that result in fewer volatile organic compound (VOC) and toxic air emissions than traditional coating emissions. Among the new products and improvements focused on were an electrophoretic urethane coating, a zero-VOC house paint, and developments involving such inorganic polymers as zinc silicates and silicones. Coatings for such substrates as metal (aerospace), wood (furniture), plastic, foil, and concrete were also discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS			
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Coatings	Stationary Sources	11C	
Coating Processes Volatile Organic Com-		13H	
Emission pounds (VOCs)		14G	
Organic Compounds		07C	
Volatility	·	20 M	
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